

FINAL REPORT

INVESTIGATION OF THE REACTION OF TITANIUM WITH HYDROGEN

by

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Your personal interest and helpful comments during the course of this investigation have been greatly appreciated. We trust that the results obtained will prove useful in furthering the space program.

Very truly yours,

Edwin S. Bartlett  
Chief  
Nonferrous Metallurgy Division

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## FORWARD

Hydriding of unalloyed titanium tubing has been found in a system which delivers gaseous hydrogen from a liquid hydrogen storage tank. In order to learn the cause of this hydriding and methods of preventing it, NASA Manned Spacecraft Center, Houston, Texas, initiated a study at Battelle Memorial Institute, Columbus Laboratories. This work was performed under NASA Contracts NAS 9-5298, 9-6565, and 9-7549 during the periods October, 1965, to June, 1966; October, 1966, to April, 1967; and January to December, 1968.

In a second phase of Contract NAS 9-7549 conducted from January to December, 1968, a study of hydrogen-related weld embrittlement in titanium alloy weldments was conducted. This study was initiated at Battelle as a result of a failure of a Ti-6Al-4V helium pressure vessel of a Saturn IV B rocket tentatively attributed to hydrides in the weld area. The conditions leading to hydride formation in Ti-6Al-4V weldments made with unalloyed filler metal were investigated.

These studies were administered under the direction of Mr. S.V. Glorioso, NASA/MSC. Battelle personnel who participated in the investigation were E. S. Bartlett, Chief; D. N. Williams, Associate Chief; A. W. Hodge, Fellow (now retired); and B. G. Koehl, Chemist; all of the Nonferrous Metallurgy Division. R. A. Mueller of the Materials Joining Technology Division supervised the welding operations.

## INVESTIGATION OF THE REACTION OF TITANIUM WITH HYDROGEN

### ABSTRACT

An investigation of the reaction between titanium and hydrogen gas has been made to determine the factors which promote surface hydriding and methods of preventing it. A second phase of the work studied weld embrittlement resulting from hydrogen segregation in sheets of Ti-6Al-4V alloy welded with unalloyed titanium filler metal.

High-purity hydrogen was essential for a reaction to occur between titanium and hydrogen gas in these studies. At near room temperature and a hydrogen pressure up to 20 psig, a clean, vacuum annealed surface was found to be essential for hydriding. Above 20 psig hydrogen pressure, only abrasion or galling immediately preceding hydrogen exposure was needed to initiate the reaction. An increase in hydrogen pressure or temperature, an acicular microstructure, and oily contamination during galling or abrasion all increased the tendency toward reaction with hydrogen. Reaction was decreased by exposure of specimens to air after abrading or galling and before hydrogen exposure. Stress had no effect in initiating a reaction nor did length of exposure time.

In 35 percent dilution welds of Ti-6Al-4V plates using unalloyed titanium (Ti-50A) filler material, no significant evidence of hydrogen embrittlement was found in mechanical property studies, although hydride banding was observed.

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## SUMMARY

This work was done in two phases, (1) Gas-Metal Reactions, and (2) Weld Embrittlement Studies

### Gas-Metal Reactions

The purpose of this investigation was to determine whether titanium and titanium alloys could be made to react consistently with hydrogen at near room temperatures and low to medium pressures. After determining the factors which influenced this reaction, methods for decreasing the susceptibility of titanium and its alloys to reaction with hydrogen were studied.

The factors which were studied and the effect of these factors on the titanium-hydrogen reaction at near room temperature and at low to medium hydrogen pressure were as follows:

Hydrogen Purity. For a reaction between hydrogen gas and titanium to occur in these studies, hydrogen of highest purity trapped with liquid nitrogen was necessary. The oxygen impurity found in less pure hydrogen contaminated the sample surface thus preventing the hydriding reaction.

Pressure. Reaction between titanium and hydrogen occurred at pressures from atmospheric to 1000 psig depending on surface treatment of the sample. Below a hydrogen pressure of 20 psig, the surface required vacuum annealing to produce a surface sufficiently clean to react with hydrogen. Above 20 psig hydrogen pressure, only galling or abrasion immediately preceding exposure was needed to initiate a hydriding reaction. A definite correlation was found between hydride thickness and hydrogen pressure.

Temperature. Most of the work was done at temperatures from 75 to 130 F and little, if any, difference in hydriding rate with temperature within this range was noted.

Surface Condition. The oxide layer, always present on titanium surfaces, was a critical factor in hydriding. Its removal by abrasion or galling and vacuum annealing (with a titanium foil getter), assured hydriding at atmospheric hydrogen pressures. Above 20 psig, only abrading or galling was necessary. Exposure of the abraded and annealed surface to air for only one minute eliminated hydriding completely at atmospheric hydrogen pressure. At above atmospheric pressures, the amount of hydriding decreased with increasing exposure to air after abrasion and before hydrogen exposure. Some time between one and six days' air exposure was sufficient to inhibit hydriding.



Stress. The effects of both cyclic and static stress on the initiation of the titanium-hydrogen reaction were studied at atmospheric and 300 psig hydrogen pressures. Neither type of stress had any effect on the reaction with hydrogen. Cyclic stress appeared to promote hydride spalling and surface pitting on one test.

Galling. All the metallic material used in the work to scratch or gall the titanium resulted in initiating a hydriding reaction. These materials included Ti-50, H-11 steel, 304 SS, C-3 tool, iron, nickel, and a wire brush. Hydriding tended to occur only in the vicinity of the scratches produced by galling and not over the entire surface. The intensity of the reaction was not appreciably affected by the manner of the galling (longitudinal, transverse, or by lathe) nor was it affected by the material used to gall the titanium. The mere contact of a material (iron and nickel) with the titanium was not proved conclusively to have initiated a hydrogen reaction.

Contamination. When titanium was galled in the presence of various contaminants, the hydrogen reaction was considerably increased. Among the contaminants found, oil was most intensively studied because of its common presence in industrial processes. Oily contamination reduces the effectiveness of air exposure in retarding hydriding. After six days in air following oily galling, the hydrogen reaction still occurred although not as extensively as noted immediately after galling. Oily contamination also increases the tendency for galling to initiate a reaction.

Material Composition. Ti-50A, Ti-5Al-2.5Sn, Ti-6Al-4V, and Ti-13V-11Cr-3Al titanium alloys were used in this work. The most reactive with hydrogen was Ti-13V-11Cr-3Al; however, it was only tested at atmospheric pressure. After the Ti-13V-11Cr-3Al reaction at atmospheric pressure, Ti-5Al-2.5Sn proved to be the next most reactive, only slightly more so than the Ti-50A. Ti-6Al-4V was the least reactive. At 300 psig hydrogen pressure, the Ti-5Al-2.5Sn alloy was most reactive followed by Ti-50A. The Ti-6Al-4V proved to be least reactive at the higher hydrogen pressure.

Material Structure. The coarse acicular microstructure proved to be the most reactive with hydrogen and least affected by exposure to air after abrasion and prior to hydrogen exposure. There was little difference in hydrogen reactivity among the samples having equiaxed and cold rolled microstructures.

Time. The time of evacuation before exposure to hydrogen proved to be of little significance. The time of exposure to air after abrasion and prior to hydrogen exposure was very important, increased time of exposure resulting in decreased hydrogen reaction.

Galling in a Hydrogen Atmosphere. Galling in a hydrogen atmosphere resulted in a rapid hydriding of the galled surfaces and accelerated wear of the titanium.

### Weld Embrittlement Studies

This phase of the work was designed to determine the effect of hydrogen segregation and subsequent weld embrittlement in welds made in Ti-6Al-4V using unalloyed titanium as filler metal.

Four weldments were made of Ti-6Al-4V sheets welded with Ti-50A filler metal and one of Ti-6Al-4V sheets welded with Ti-6Al-4V filler metal. All welds were of about 35 percent dilution\*. The hydrogen content of the Ti-6Al-4V sheets varied from 63 to 313 ppm and that of the Ti-50A from 64 to 145 ppm.

Metallographic examination showed hydride precipitation in all the welds except the one which consisted of Ti-6Al-4V welded with Ti-6Al-4V filler metal. Bands of hydride were observed at the weld metal-heat affected zone interface of welds made to join high hydrogen Ti-6Al-4V sheet using unalloyed titanium filler metal. The amount of banding was heavier in a weld made using high hydrogen unalloyed titanium filler, but was also present in a weld using low hydrogen unalloyed titanium filler.

Notched tensile tests, unnotched tensile tests at two strain rates, notched stress rupture tests, and sustained bending load tests failed to show significant evidence of hydrogen embrittlement, either impact embrittlement or low strain rate embrittlement.

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\*As defined in the AWS Handbook.

## STUDIES OF THE REACTION BETWEEN HYDROGEN GAS AND TITANIUM

### Introduction

This investigation was started as a result of the failure of a titanium tank which was attributed to a reaction between titanium and hydrogen gas near room temperature<sup>(1)</sup>. Liquid hydrogen storage tanks intended for spacecraft use were made of double-wall welded Ti-5Al-2.5Sn alloy. These tanks have three connecting tubes of unalloyed titanium for use in filling and venting liquid hydrogen and discharging gaseous hydrogen. Ti-5Al-2.5Sn fittings were welded to the external ends of these tubes to permit attachment to hydrogen lines.

Failure occurred during the acceptance testing of these tanks. As part of the acceptance test sequence, the tanks were heated to 140 F, filled with liquid hydrogen, held under a gas pressure of 300 psi, and then evacuated, the entire cycle being repeated a number of times. First failures were observed after about 50 thermal cycles or about 250 hours exposure time. Later, failures were observed in as few as 1 to 10 cycles with the tanks pressurized about 2/3 of the time.

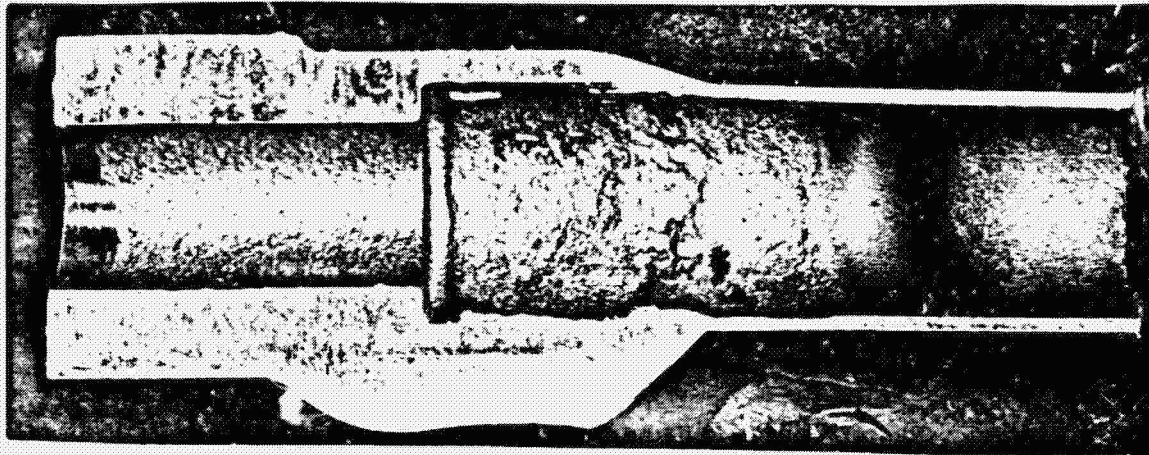
Severe erosion and pitting of the tubing occurred in the vicinity of the welds, as shown in Figure 1, in areas exposed predominantly to gaseous hydrogen. Pitting was so severe as to lead to perforation of the tube wall on several of the tanks. The pitting was the result of the spalling of surface hydrides formed by reaction between hydrogen gas and titanium. Metallographic study showed hydriding along a considerable portion of the interior surface of some of the tubing, as far as 7 inches from the nearest weld. The hydride in this case was generally present as a thin continuous layer, as shown in Figure 2. No problems were encountered in areas of the tanks exposed to gaseous hydrogen at temperatures and pressures which did not exceed 150 F and 300 psi, respectively.

Little is known of the reaction of hydrogen gas with titanium and its alloys at moderate temperatures and pressures. In view of the contemplated use of titanium and its alloys in liquid hydrogen tanks and other critical components where exposure to high-pressure hydrogen gas is anticipated, it was desirable to determine the factors that affected the reaction of gaseous hydrogen with titanium and titanium alloys and to determine whether the failure of the liquid hydrogen storage tank was an isolated occurrence resulting from an unusual set of circumstances or whether reaction between titanium and gaseous hydrogen near room temperature is to be expected under normal conditions.

A number of factors can influence the reaction between titanium and hydrogen gas. These include the purity and pressure of the hydrogen gas; material characteristics such as surface condition, alloy composition, and microstructure; the reaction temperature; and the reaction time. Each

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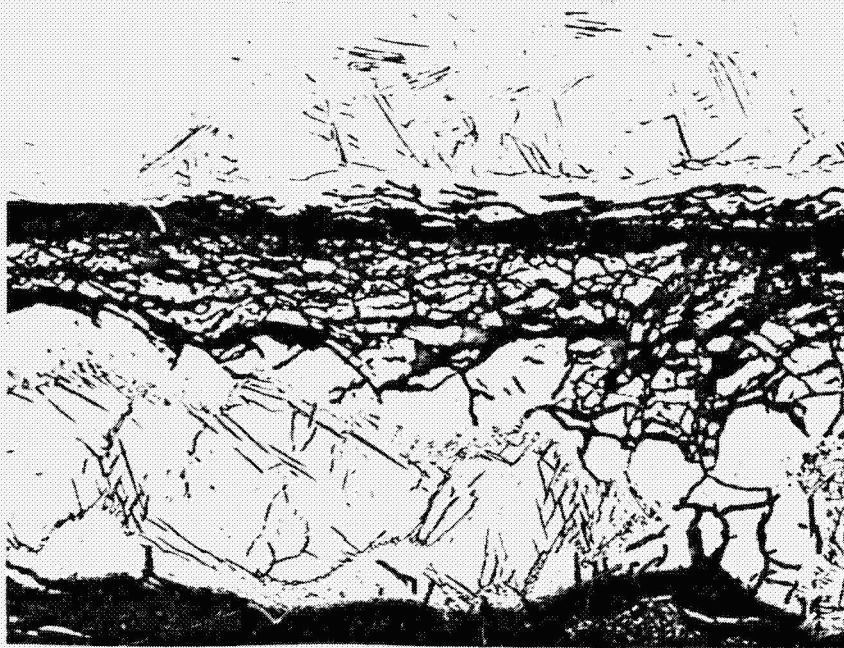
(1) Williams, D.N., and Maykuth, D.J., "Reaction of Titanium with Gaseous Hydrogen at Ambient Temperatures", DMIC Technical Note, Defense Metals Information Center, Battelle Memorial Institute (February 4, 1966).



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(a) Photograph of a tank fitting after sectioning to show internal attack



200X

22473

(b) Localized heavy hydriding near weld area of tank fitting

Figure 1. FAILED UNALLOYED TITANIUM TUBING FROM LIQUID HYDROGEN TANK

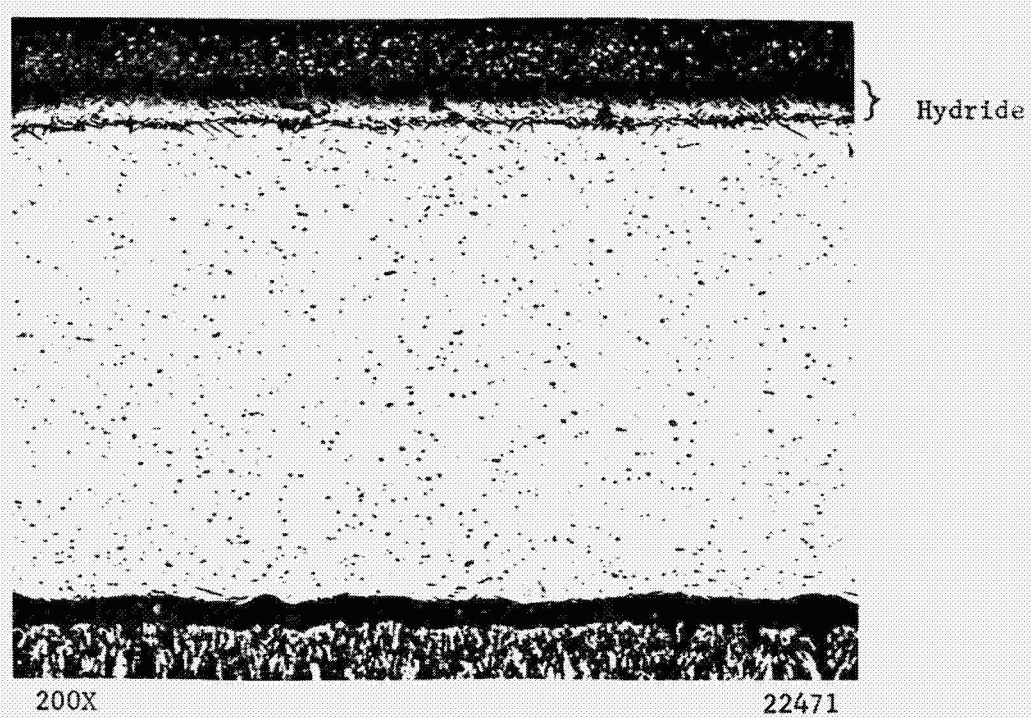


FIGURE 2. HYDRIDE ON INSIDE SURFACE OF UNALLOYED  
TITANIUM TUBE

Hydride averaged 1.2 mils in thickness.

of these factors was examined separately insofar as possible. Their effects on the reaction, as measured either by the increase in hydrogen content as determined by analysis or the thickness of surface hydride formed as determined by metallographic examination, were determined. The results of these studies are discussed in the following sections.

### Material

Titanium and titanium alloy sheet and rod were used in this work. Sheet samples were used in all the work except that which investigated the effect of galling and surface contamination on the titanium-hydrogen reaction and in studies made to prevent this reaction. To study the influence of galling, rod specimens were used.

All the sheet material, and the Ti-50A rod, was obtained from Titanium Metals Corporation of America (TMCA), while the Ti-5Al-2.5Sn and Ti-6Al-4V rod were both obtained from the Astro Metallurgical Corporation. The analyses of all the "as-received" material are given in Table 1. The most important features of these analyses were the hydrogen contents. These were checked at Battelle by the Vacuum Fusion method. The certified analyses accompanying the material and the analyses made at Battelle agreed closely except for the hydrogen content of the Ti-5Al-2.5Sn and Ti-6Al-4V rod. Repeated analyses at Battelle showed  $19 \pm 1$  and  $37 \pm 1$  ppm hydrogen for the Ti-5Al-2.5Sn and Ti-6Al-4V alloys, respectively, instead of the 6 and 5 ppm hydrogen, respectively, given by the producer. The hydrogen content of the Ti-5Al-2.5Sn and Ti-6Al-4V alloys were taken as the values found at Battelle.

Samples were prepared in a variety of sizes and heat treated conditions. These sizes and conditions and specific studies for which they were used are summarized in Table 2. Figure 3 shows typical microstructures examined in this work.

The heat treatments were carried out in argon-filled Vycor capsules in the following manner:

#### Ti-50A (Rod and Sheet)

- (1) Annealed 1/2 hour at 1750 F and slow cooled\* to produce a coarse acicular alpha microstructure.
- (2) Annealed 1/2 hour at 1200 F and air cooled to produce a fine-grained equiaxed alpha microstructure.
- (3) Annealed 1/2 hour at 1750 F and water quenched to produce a fine acicular alpha structure.
- (4) No heat treatment; samples were cold rolled 53 percent.
- (5) No treatment (mill annealed equiaxed structure).

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\* Capsules containing the samples were buried in vermiculite insulation to insure slow cooling.

TABLE 1. ANALYSES OF THE TITANIUM AND TITANIUM ALLOYS USED IN THIS WORK

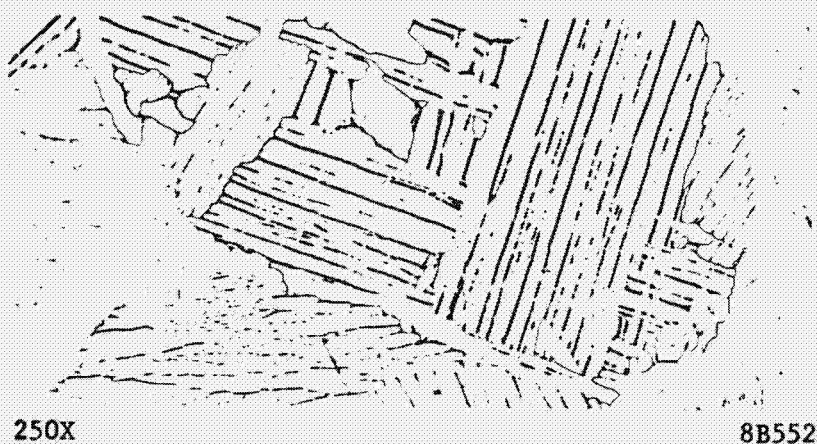
Alloy	Percent by Weight								
	C	Fe	Al	V	Cr	Sn	H	O	N
<u>Sheet Material</u>									
Ti-50A	0.023	0.10	--	--	--	--	0.003	0.11	0.012
Ti-75A	0.025	0.15	--	--	--	--	0.004	0.33	0.019
Ti-5Al-2.5Sn ELI	0.023	0.12	5.2	--	--	2.4	0.009	0.08	0.013
Ti-6Al-4V ELI	0.023	0.12	5.9	3.9	--	--	0.007	0.08	0.013
B-120-VCA	0.019	0.16	3.1	13.6	11.1	--	0.016	0.17	0.028
<u>Rod Material</u>									
Ti-50A	0.025	0.08	--	--	--	--	0.0050	0.14	0.011
Ti-5Al-2.5Sn	0.015	0.095	5.26	--	--	2.69	0.0019	0.10	0.017
Ti-6Al-4V ELI	0.015	0.088	6.08	4.11	--	--	0.0037	0.12	0.010

TABLE 2. SUMMARY OF MATERIAL SIZE AND MICROSTRUCTURE FOR VARIOUS EXPERIMENTS

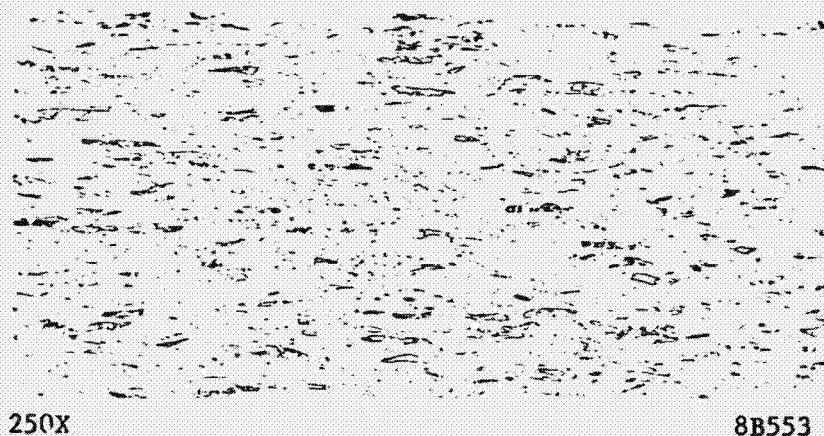
Purpose of Experiment	System	Pressure	Material	Microstructure	Dimensions, inches		
					Length	Width	Thickness
Effect of surface cleanliness (abrasion annealing, etc.)	Glass	Atmospheric	Ti-50A	Acicular	1 to 3	3/4	0.032
			Ti-75A	Equiaxed			
			Ti-5Al-2.5Sn	Acicular			
			Ti-6Al-4V	Acicular			
			B-120-VCA	Acicular			
Effect of cyclic stress	"	"	Ti-50A	Acicular	3	3/4	0.015
			Ti-6Al-4V	Acicular			
			Oxidized Ti-50A	Acicular			
Effect of pressure, oxide surface layer and air exposure	Stainless steel pressure chamber	Above atmospheric	Ti-50A	Acicular	2	1/2	0.015
			Ti-6Al-4V	Equiaxed Cold rolled Acicular			
Effect of static stress	Ditto	Ditto	Ti-50A	Acicular	1-1/4	1/2	0.015
			Ti-6Al-4V	Equiaxed Cold rolled Acicular			
Effect of galling and contamination	"	"	Ti-50A	Acicular	1/8-inch diameter x 2-inches long rod		
			Ti-5Al-2.5Sn	Acicular			
			Ti-6Al-4V	Acicular			
Effect of cyclic stress	Standard high pressure autoclave, modified	"	Ti-50A	Equiaxed Acicular	2-11/16	0.19	0.032
Effect of pressure, temperature, and time	Stainless steel capsules	"	Ti-50A	Equiaxed Acicular (coarse) Acicular (fine) Several with weld bead on acicular	4	3/4	0.032
Effect of pressure on "as-received"	Stainless steel pressure chamber	"	Ti-55A	Equiaxed	1-1/2	0.28-inch OD 0.22-inch ID tubing	



(a) Ti-50A  
Coarse acicular  
structure



(b) Ti-50A  
Cold-rolled  
structure



(c) Ti-50A  
Fine equiaxed  
structure

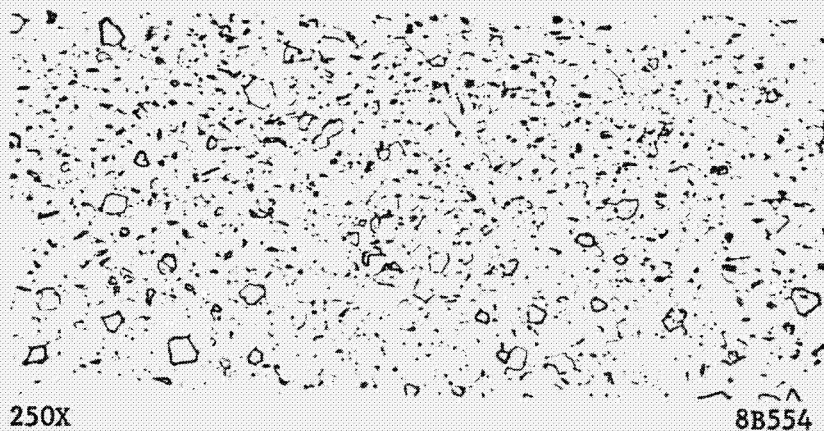


FIGURE 3. MICROSTRUCTURES OF FIVE OF THE TITANIUM MATERIALS USED IN THIS WORK

(d) Ti-6Al-4V  
Coarse acicular  
structure



(e) Ti-5Al-2.5Sn  
Coarse acicular  
structure

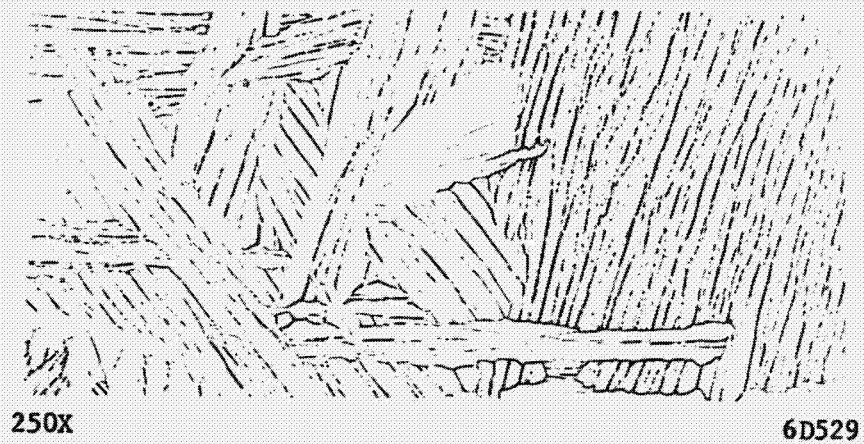


FIGURE 3. (continued)

Ti-5Al-2.5Sn

- (1) Sheet, "as-received", no treatment (mill annealed equiaxed structure).
- (2) Rod, annealed 1/2 hour at 2060 F and slow cooled to produce a coarse acicular structure.

Ti-6Al-4V

- (1) Sheet, annealed 1/2 hour at 1950 F and slow cooled to produce a coarse acicular alpha microstructure.
- (2) Rod, annealed 1/4 hour at 1740 F and water quenched to produce a 50 percent equiaxed alpha structure in a martensitic matrix.

Some of the Ti-50A was exposed to air for varying lengths of time and at various temperatures to produce surface oxide layers of various thicknesses. The treatments used and the oxide thicknesses produced are shown in Table 3.

A short length of Ti-55A tubing (7 mm OD, 5-1/2 mm ID), part of the same lot of material used in the lines of a liquid-hydrogen tank discussed in the introduction, was also examined. This material was supplied in the "as-received" condition and had an equiaxed alpha microstructure.

All material except the tubing sample was degreased with cp\* acetone before annealing. After annealing and before abrading or galling, the samples were etched with a solution of 67 parts H<sub>2</sub>O, 33 parts HNO<sub>3</sub>, and 3 parts HF. The tubing was used in the "as-received" condition.

Hydrogen gas was obtained from the Matheson Company. Ultrapure-grade hydrogen with a dewpoint of lower than -80 F and impurities of <1 ppm O<sub>2</sub>, <5 ppm N<sub>2</sub>, and <1 ppm total hydrocarbons (as CH<sub>4</sub>) was used in all of this work.

Experimental Equipment and TechniqueAtmospheric Pressure Studies

All of the experimental work at one atmosphere pressure of hydrogen was done in a Vycor reaction tube attached to the glass vacuum system shown schematically in Figure 4.

A mechanical pump, a glass mercury diffusion pump, and a cold trap made up the pumping system. A full-length, open-end, mercury manometer was connected in the pump-out line and was used to measure pressure change during

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\*cp - chemically pure.

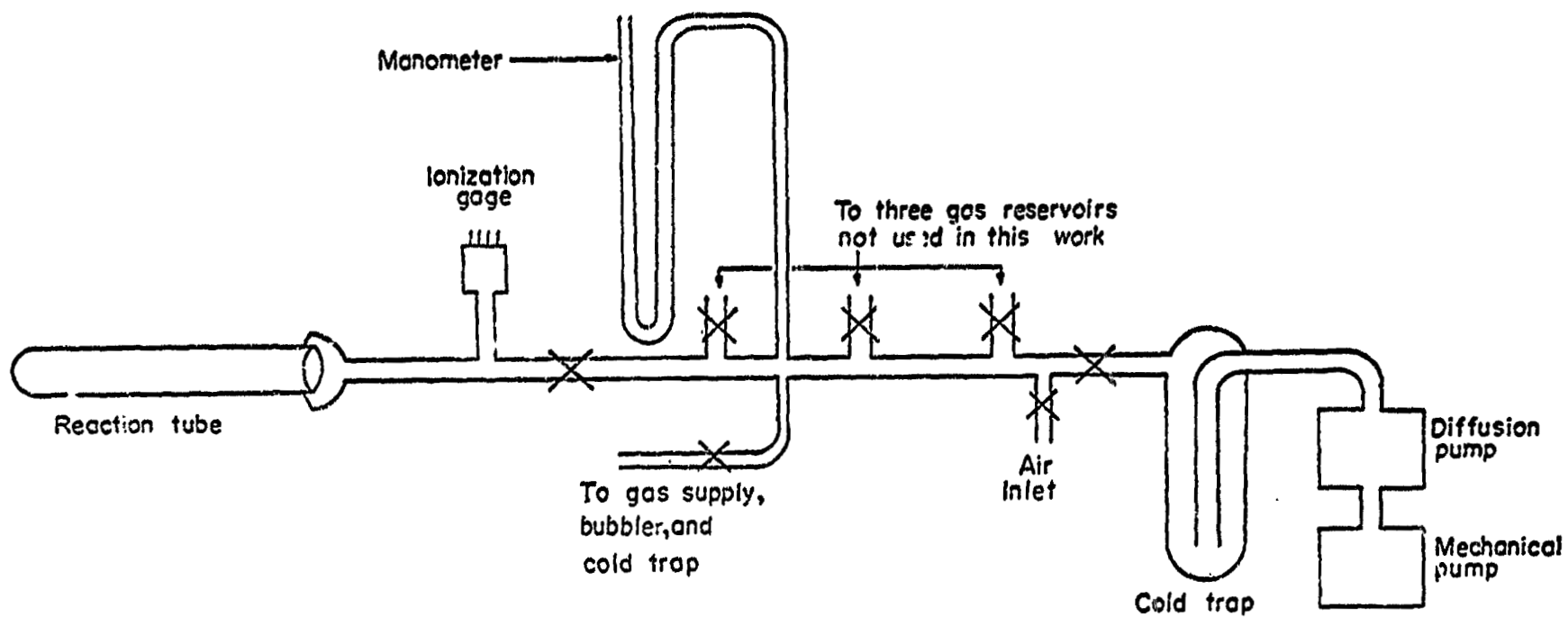
TABLE 3. TREATMENTS USED TO OXIDIZE TEST SAMPLES

Oxidation Treatment		Weight Gain, gm/sq.in.	Calculated Oxide Thickness, microinches <sup>(a)</sup>
Time, hours	Temperature, F		
6	1150	0.00079	11
6	1150	0.00081	12
6	1150	0.00102	15
10	1150	0.00142	20
10	1150	0.00151	22
15	1150	0.00197	28
30	1150	0.00400	57
1	1450	0.00521	75
5 minutes	1800	0.01041	149

(a) Calculation method:

$$\text{Oxide film thickness in microinches} = \frac{\text{Weight gain in grams}}{\text{Surface area (in.}^2\text{) of sample}} \times \frac{1}{69.82}$$

This assumes that: All oxygen absorbed is utilized in forming oxide, and the oxide is rutile,  $\text{TiO}_2$  with density of 69.82 gm/in<sup>3</sup>.



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FIGURE 4. DIAGRAM OF GLASS SYSTEM

the experimental runs. The quantity of hydrogen reacted during an experimental run was easily calculated from the pressure change in the calibrated volume of the system. An ionization gage was used to monitor the system during evacuation and annealing operations. The samples contained in the reaction tube were heated by a resistance furnace monitored by a Foxboro Controller. Samples were annealed only after evacuation of the system to a pressure of about 0.05 micron or lower with a leak rate of about 0.02 micron/minute.

The same glass system was used both for experiments on unstressed samples and for experiments on samples that were stressed during exposure to hydrogen at atmospheric pressure. To obtain stress on samples the samples were bolted between two identical sections of Type 304 stainless steel. A full-scale sketch of the sample holder is shown in Figure 5. One sample holder was machined to a 2.54-inch radius over which the samples were bent to provide a maximum strain in 15-mil sheet of 0.3 percent, equivalent to a stress of about 50,000 psi. The second sample holder was machined to a 0.75-inch radius to provide a maximum fiber strain of 1.0 percent, which would provide appreciable plastic flow on the sample surface.

Flexing to stress the sample was produced by two large permanent horseshoe magnets mounted on a moveable platform as shown in Figure 6. A 1-rpm electric motor oscillated this platform first in one direction, then the other, resulting in one complete cycle of strain (maximum tension through maximum compression and return) per minute. Because titanium is nonmagnetic, small copper-plated steel plates were bolted to each side of the sample at the end which was free to flex. Heating tape was used in the experimental runs made above room temperature.

#### Studies at Greater Than 1 Atmosphere Pressure

Unstressed (300 psig, near room temperature). Part of the experimental work on unstressed samples at greater than atmospheric pressures of hydrogen and near room temperature was done in the stainless steel chamber shown in Figure 7. The inside height was 11-1/2 inches and inside diameter was 5 inches. The chamber was sealed with an O-ring to a base plate in which tubing was connected for evacuation and gas addition. The outside of the chamber was wound with copper tubing through which water was circulated to maintain temperatures up to 130 F used in this work. Evacuation was accomplished through 1-inch copper lines by means of an oil diffusion pump and a mechanical pump. A vacuum of about 0.03 microns was obtained before the addition of the hydrogen and was read on a Consolidated Electrodynamics Discharge Gage. Hydrogen was added through a liquid nitrogen trap and the pressure was read on a 10-inch Heise Bourdon gage with readings accurate to 1 psig. The samples were exposed to hydrogen in groups of up to 24 at one time. The samples were individually held on a glass rack.

The same chamber was used for galling the samples while under hydrogen pressure by means of the equipment shown in Figure 8. (This equipment is shown in place on the stainless steel chamber in Figure 7.) The test sample was mounted on the driven rod and the galling or abrading material on the hinged mount. Reciprocating motion to produce galling was

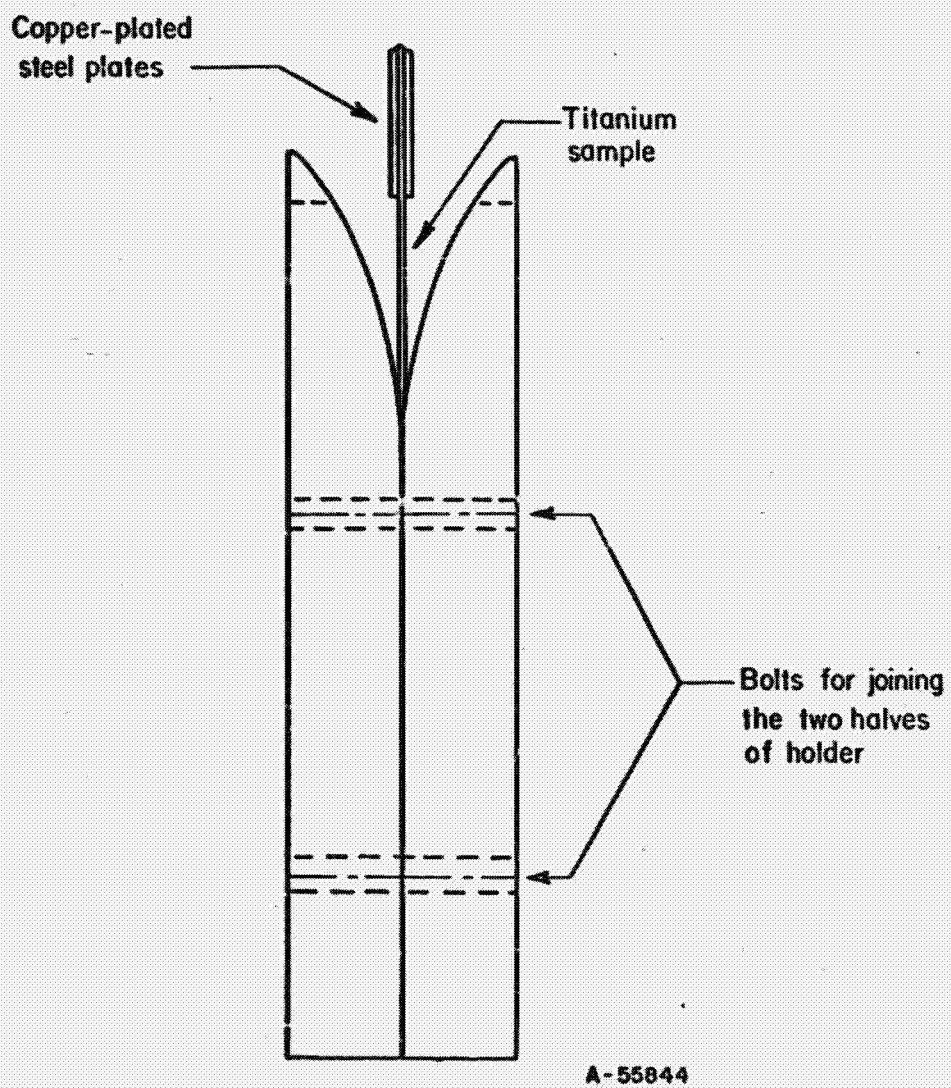
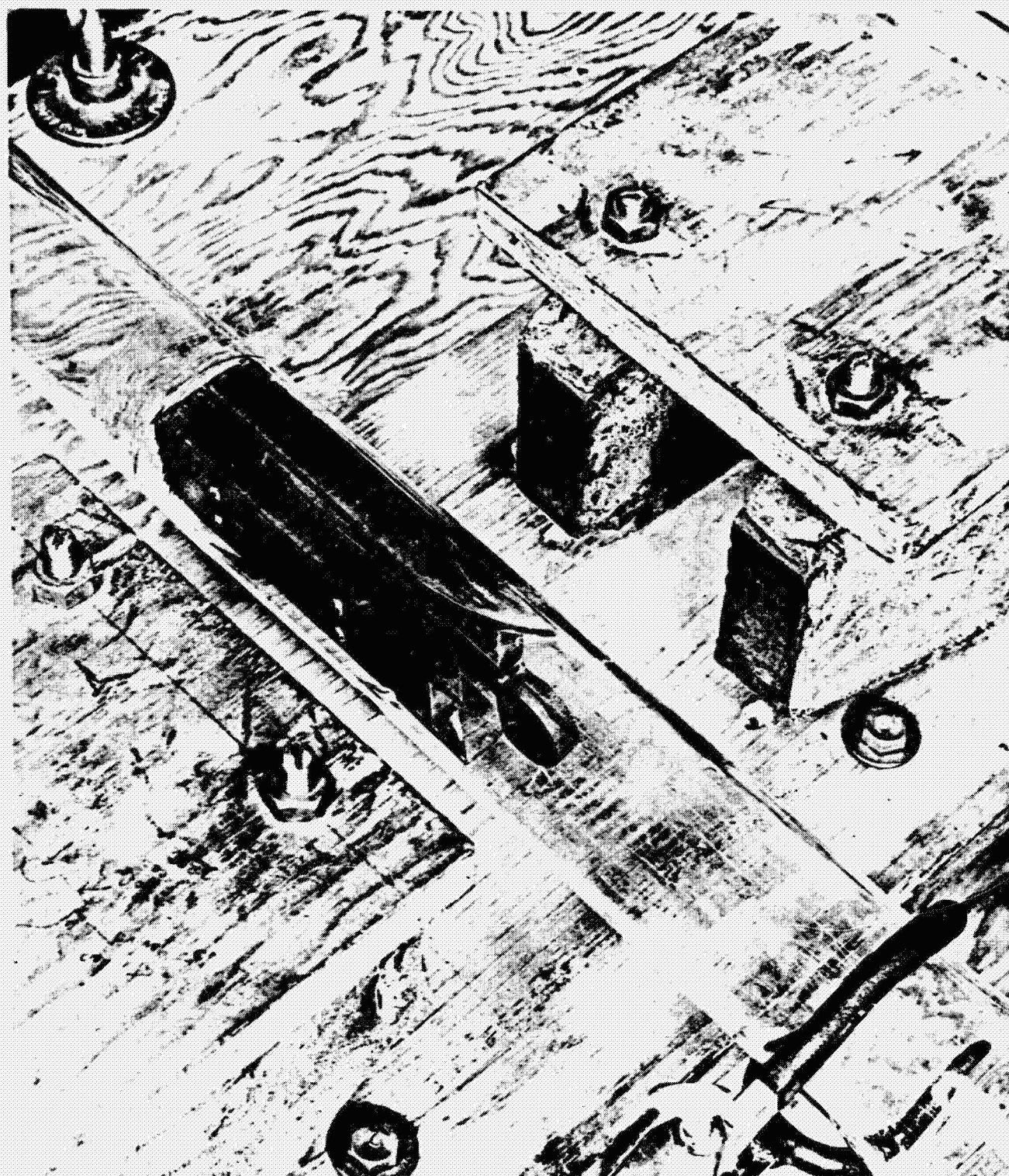


FIGURE 5. FULL-SCALE SKETCH OF SAMPLE HOLDER FOR APPLYING STRESS





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FIGURE 6. METHOD OF PRODUCING STRESS IN TITANIUM SAMPLE IN GLASS SYSTEM

Sample is shown bolted in holder inside the Vycor reaction tube positioned between the two oscillating magnets. This was part of the glass vacuum system.



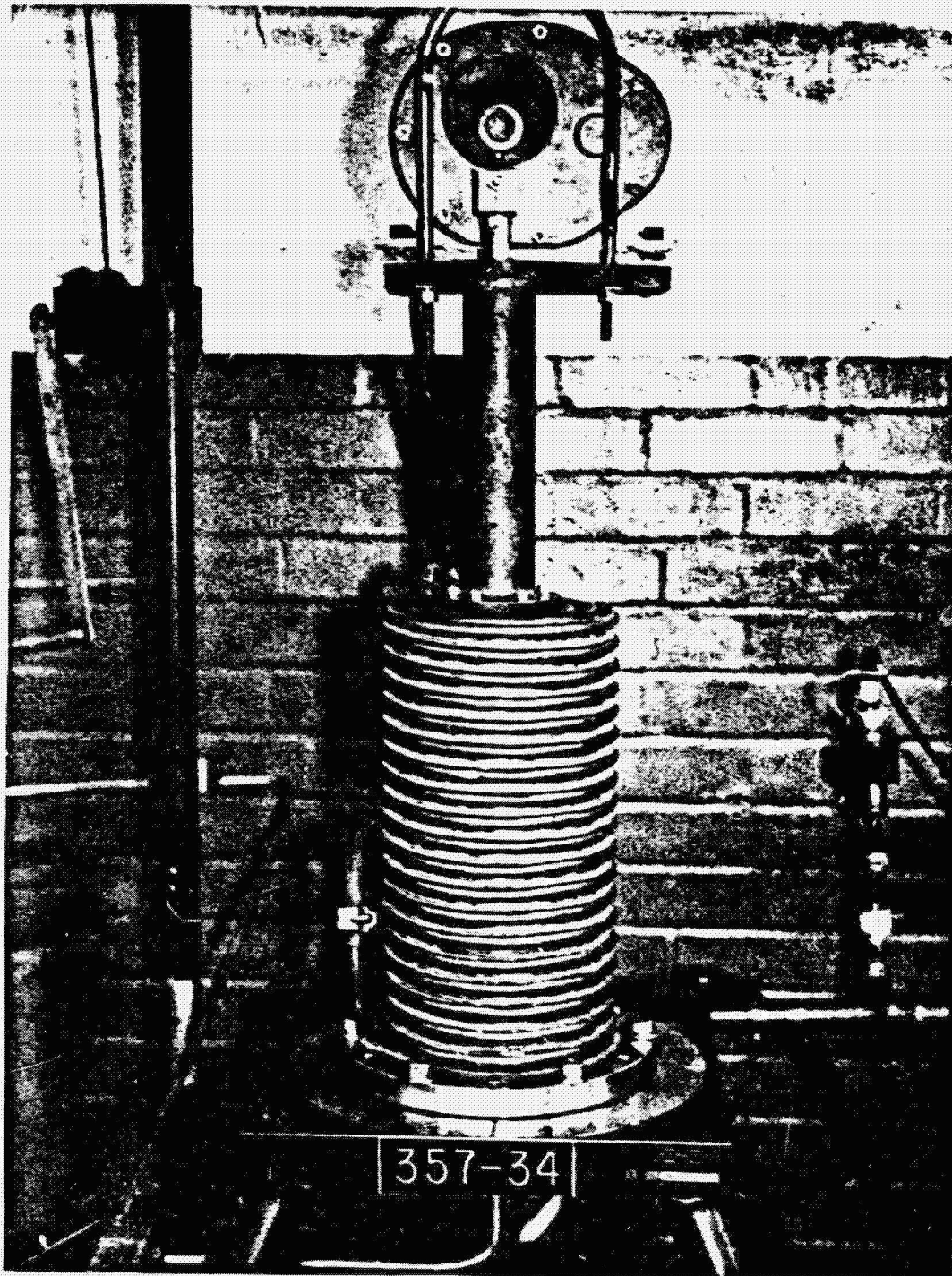


FIGURE 7. APPARATUS USED FOR WORK ABOVE ATMOSPHERIC PRESSURE

The lower section was used for hydrogen exposure of stationary samples. The upper section was added in order to gall samples while under pressure.

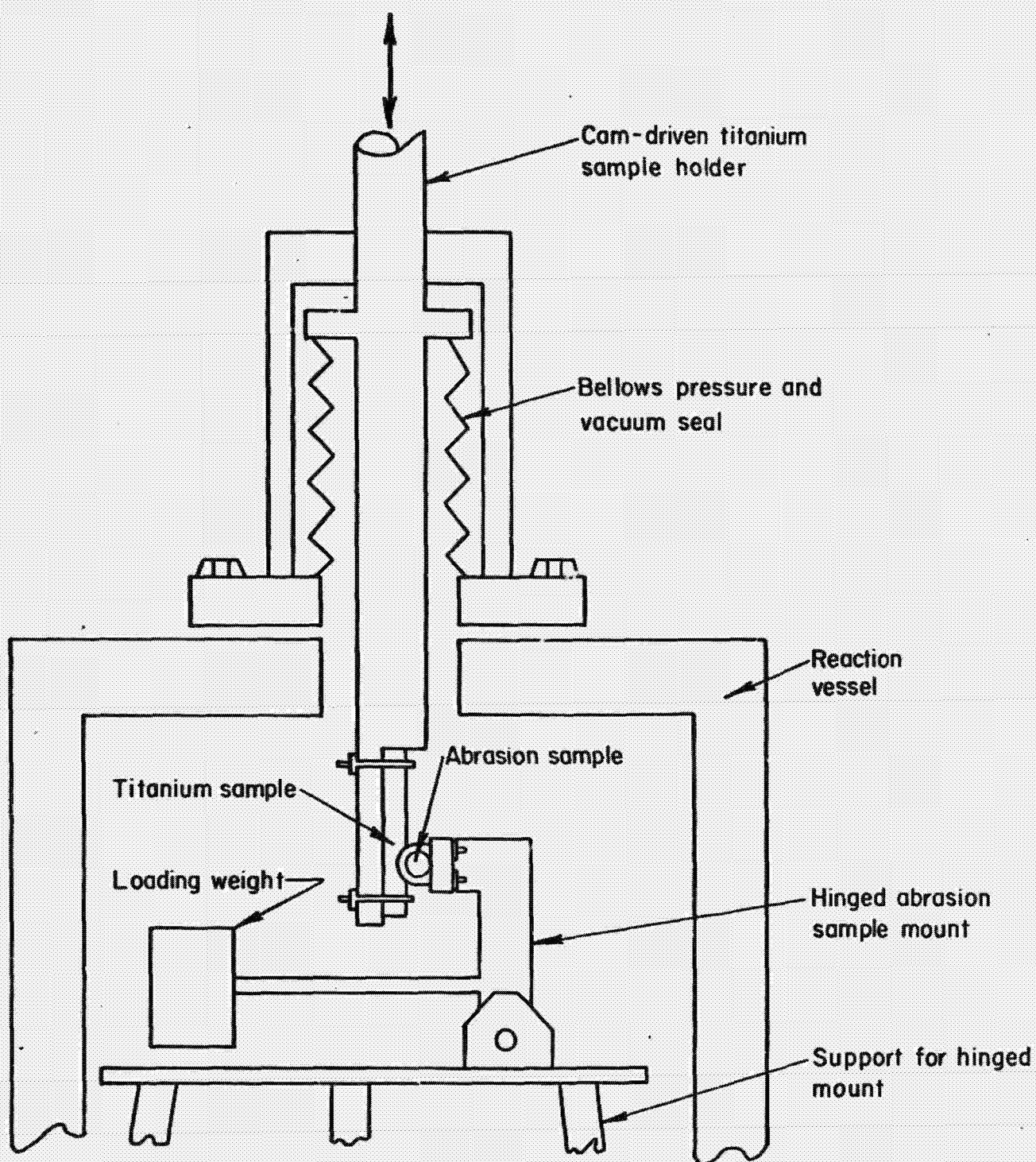


FIGURE 8. DRAWING OF DEVICE TO PERMIT GALLING OF SAMPLE IN A HYDROGEN ATMOSPHERE

transmitted from a 30-rpm motor through a cam to the bellows-sealed sample holder. A single wear scar was produced on the sample and a notch was worn into the stationary galling material.

The effects of pressure, temperature, and time of exposure of unstressed titanium to hydrogen were also studied in a series of experimental runs using an entirely different technique than that described above. Samples were sealed in stainless steel capsules (3 samples to a capsule, 1 inch ID and 10 inches long) with a 4-foot length of pressure tubing welded to one end. This tubing was to facilitate evacuation during annealing in a large muffle furnace. The samples were evacuated to about 5 to 10 microns pressure and heated 2 hours at 1500 F. After cooling in a vacuum, the capsules were transferred to a manifold where they were filled with ultrapure hydrogen trapped with liquid nitrogen.

After filling with hydrogen, the capsules containing the titanium samples were removed from the manifold and transferred to one of two oil baths maintained at 300 and 170 F, respectively. For the experiment at 75 F, the pressurized capsules were placed in a constant-temperature room maintained at 75 F.

Statically Stressed (300 psig, near room temperature). The pressure chamber was the same as that used in the unstressed tests described in the beginning of this section. To apply stress, the samples were first bent in a 75-degree V die, using a 1/16-inch radius ram. Then a stainless steel bolt was placed through the two legs of the bent samples and tightened until the legs no longer returned to their original position when the stress was removed.

Cyclically and Statically Stressed (300 psig at 300 F). These tests were carried out in the assembly illustrated in Figure 9, a modified standard high-pressure autoclave. A known load was placed on the sample by a small hand-operated hydraulic pump through a stainless steel rod connected to the sample. This rod passed through a Teflon-gasketed hole in the autoclave cover. Three strip heaters were bound to the sides of the autoclave to produce the 300 F temperature desired.

#### Lathe Galling Equipment

To gall a cylindrical titanium sample evenly and with a force which was reproducible, a small lathe was used. The tool holder section was modified so that a length of rod, to be used as galling material, could be brought to bear on the sample with a definite load. The lathe had an automatic feed attachment which permitted an even galling over nearly the entire length of the sample while it was being rotated.

The galling load could be changed by suspending various weights at varying distances along a fulcrum arm to which the galling material was attached. This equipment is shown in Figure 10. Most of the experimental runs were made using a 2-pound weight attached to the fulcrum which was equivalent to a 7-pound load acting on the sample.



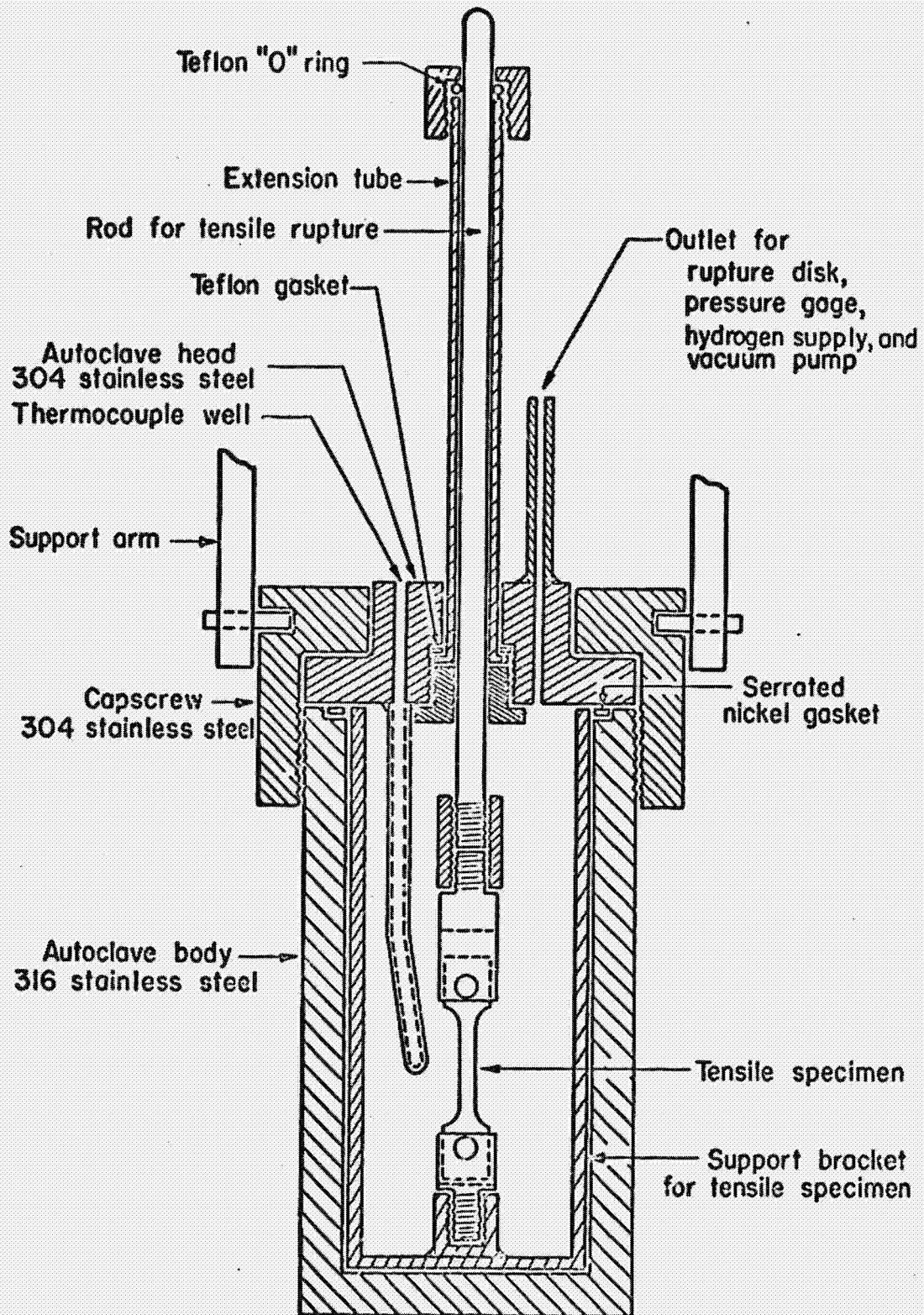


FIGURE 9. DIAGRAM OF STRESS ASSEMBLY

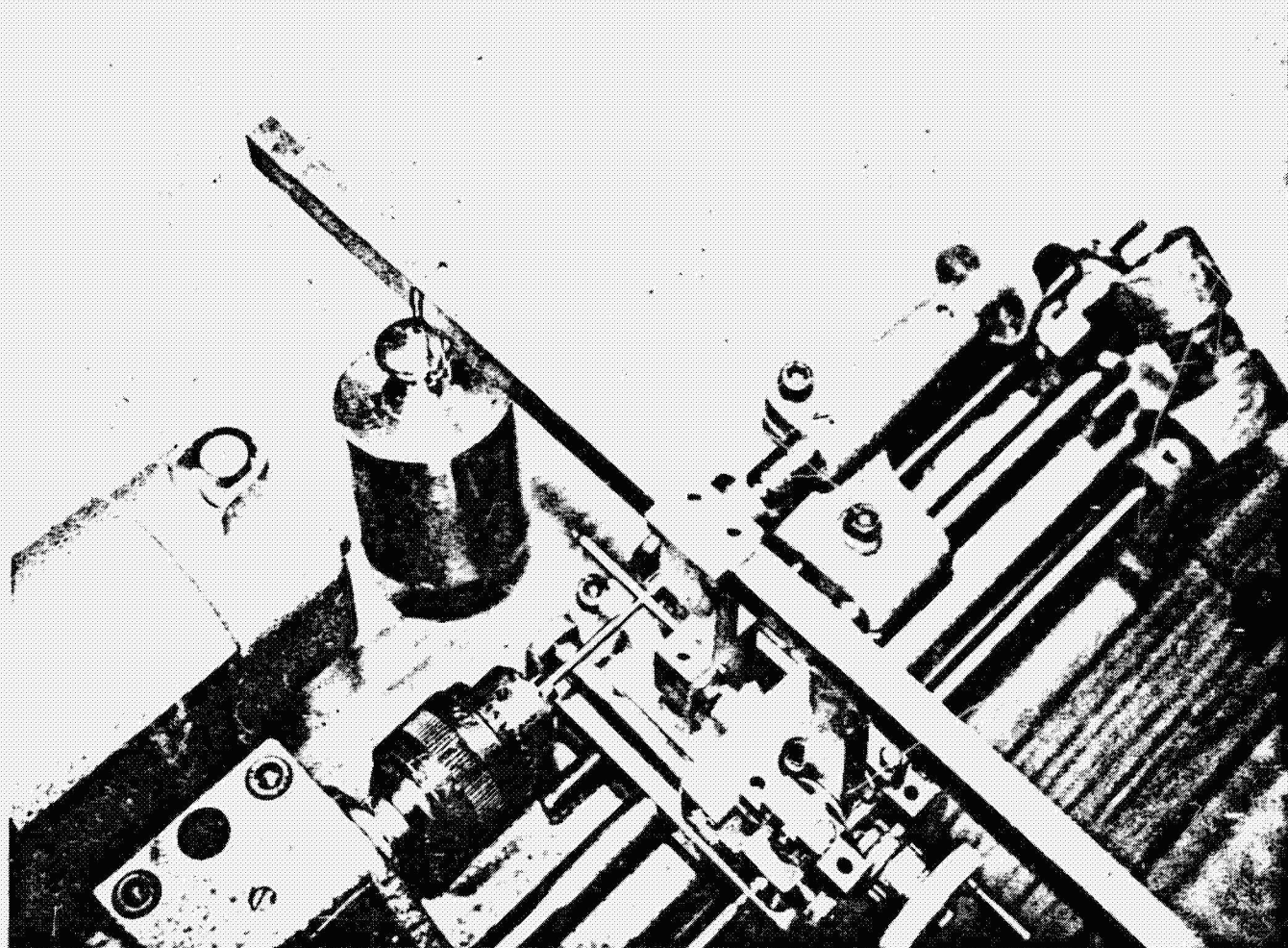


FIGURE 10. METHOD USED FOR GALLING SAMPLES IN A SMALL LATHE

## Results

In discussing the effects of the variables influencing the titanium-hydrogen reaction, their effects on the Ti-50A material having a coarse acicular structure are described unless specifically noted otherwise. This material was generally found to be quite reactive and formed an easily seen surface hydride. Several methods of detecting the reaction were used including changes in gas pressure, changes in sample weight, the thickness, location, and continuity of hydride formed as determined metallographically, and the increase in bulk hydrogen content of the sample (which was due to surface hydride in most cases). Each of these methods was of special value in some studies and of limited value in others.

### Factors Affecting the Hydriding Reaction

Hydrogen Purity. Early in the work, it was found that the purity of the hydrogen had a definite effect on the titanium-hydrogen reaction of vacuum annealed samples. The following combinations of hydrogen purity and methods of trapping to remove impurities were used to check the effect of gas purity on hydriding.

- (1) Ultrapure hydrogen, trapped with liquid  $N_2$
- (2) Ultrapure hydrogen untrapped
- (3) Commercial-grade hydrogen trapped with liquid  $N_2$
- (4) Commercial-grade hydrogen untrapped
- (5) Commercial-grade hydrogen trapped with dry ice
- (6) Commercial-grade hydrogen with increased moisture content
- (7) Commercial-grade hydrogen trapped with liquid nitrogen at about 1/3 the flow rate (25 ml/min) of the other methods.

No experimental runs were made to determine the effect of hydrogen purity on the titanium-hydrogen reaction above atmospheric hydrogen pressure.

Ultrapure hydrogen, trapped with liquid nitrogen, consistently produced a hydriding reaction at room temperature and atmospheric hydrogen pressure providing other factors (cleanliness, surface abrasion, etc.) favored a reaction. Of the other methods studied, a reaction was found only with commercial-grade hydrogen trapped with liquid nitrogen at a slow rate, about 25 ml/min.

Hydrogen gas vaporizing from liquid hydrogen is of the highest purity. It was this gas which was causing the erosion in the titanium tubing and lead to the initiation of the present program.

Commercial tank hydrogen can contain as high as 600 ppm oxygen and 2300 ppm nitrogen and has a -40 F dewpoint. Ultrahigh purity hydrogen contains <1 ppm oxygen and <5 ppm nitrogen and has a dewpoint below -80 F. A liquid nitrogen cold trap will remove both oxygen and moisture, but not nitrogen from the hydrogen, and a dry ice-acetone trap will not remove either oxygen or nitrogen but will lower the dewpoint to -80 F. Therefore, it appears that oxygen is the impurity in both grades of hydrogen which must be completely removed before a titanium-hydrogen reaction can be made to take place at atmospheric pressure.

This explanation accounts for the hydrogen reaction which occurred when commercial hydrogen was used and trapped at a very slow rate. Apparently, the oxygen impurity which contaminated the sample with its presence was completely removed by the slow flow rate through the liquid nitrogen trap.

In studies of the importance of other variables on the hydriding reaction, ultrapure hydrogen cold trapped with liquid nitrogen was used. It is possible that a reaction would occur with less pure hydrogen when other conditions are especially favorable--at high gas pressures and moderate reaction temperature, for example--and the present studies should not be inferred to show that ultrapure hydrogen is essential for a reaction to proceed.

Pressure. The effect of hydrogen pressure on the titanium-hydrogen reaction at or slightly above room temperature was examined at pressures ranging from 2 psig to 1000 psig. A hydrogen reaction took place at all pressures except 2 psig as summarized in Table 4. These reacted samples were abraded with silicon carbide paper in air immediately prior to hydrogen exposure. As indicated in a following section, to obtain a reaction at pressures near atmospheric pressure, a vacuum anneal to dissolve residual surface oxides in addition to abrasion is necessary. A more detailed discussion of the reaction with hydrogen at atmospheric pressure is found in the section on surface condition.

A definite correlation between hydrogen pressure and hydride thickness was found as shown by data for 75 and 76-1/2 hours, and 95 and 96-hour hydrogen exposure in Table 5 and Figure 11. Below 300 psig pressure, the hydride layer became discontinuous so that no accurate thickness measurement could be made.

In general, pressure does not appear to be an extremely important factor in the hydriding reaction. The importance of pressure is quite closely related to other factors, particularly to surface cleanliness where, as will be discussed in a following section, increased pressure eliminates the need for vacuum annealing to remove residual oxides and to purify the gas phase.

Temperature. Little work was done specifically to determine the effect of temperature on the reaction of titanium and hydrogen. Most of the experimental work was done at or slightly above room temperatures, 75 to 130 F, and little, if any, difference in hydrogen absorption rate was noted in this small temperature range.

TABLE 4. THE EFFECT OF PRESSURE ON THE TITANIUM-HYDROGEN  
REACTION NEAR ROOM TEMPERATURE

Hydrogen Exposure			Increase in Hydrogen Content, ppm $\pm$ 1	Description of Hydride
Temp., F	Pressure, psig	Time, hr		
95-105	2	79	10	None visible.
"	20	76-1/4	67	Thinly hydrided in isolated areas.
"	70	29	--	Thin discontinuous.
"	130	6-1/2	--	Thin discontinuous.
"	300	6	--	Thin discontinuous.
"	"	75	--	Thin continuous.
"	"	96	--	Thin continuous.
"	"	96(a)	21	A few isolated spots.
"	590	24	--	Thin discontinuous.
"	"	95	--	Heavy continuous.
"	1000	76-1/2	--	Heavy continuous.
75-90	300	30-1/2	--	Thin continuous; some deep penetration.
"	"	72	--	Thin discontinuous.
"	"	96-1/4	335	Thin discontinuous.

(a) Sample was exposed to air 24 hours after abrading and before hydrogen exposure.

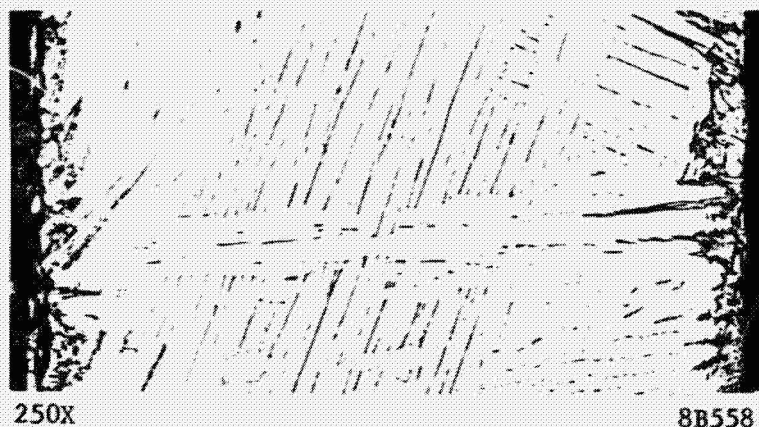
Note: Samples were dry abraded with 240-grit silicon carbide paper.



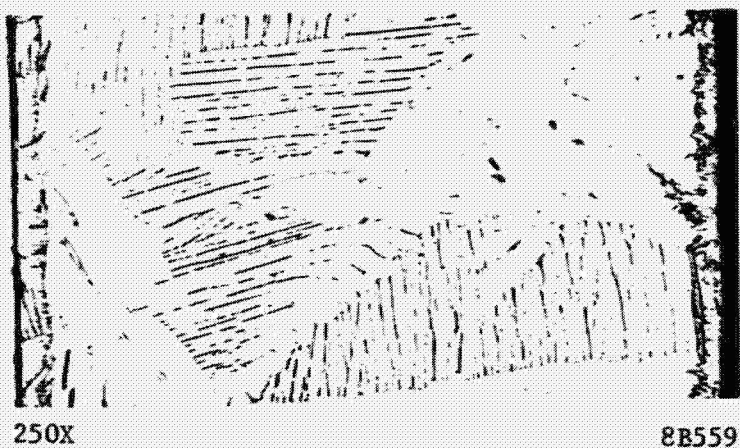
**TABLE 5. VARIATION OF THE SURFACE HYDRIDE THICKNESS WITH HYDROGEN PRESSURE**

Temp., F	Hydrogen Exposure		Thickness of Hydride, mils
	Pressure, psig	Time, hr	
95-105	300	75	0.37
95-105	300	96	0.49
95-105	590	95	0.61
95-105	1000	76-1/2	0.73

- (a) Exposed to 1000 psig hydrogen pressure for 76-1/2 hours, average hydride thickness 0.73 mil (note deep penetration)



- (b) Exposed to 590 psig hydrogen pressure for 95 hours, average hydride thickness 0.61 mil



- (c) Exposed to 300 psig hydrogen pressure for 96 hours, average hydride thickness 0.49 mil

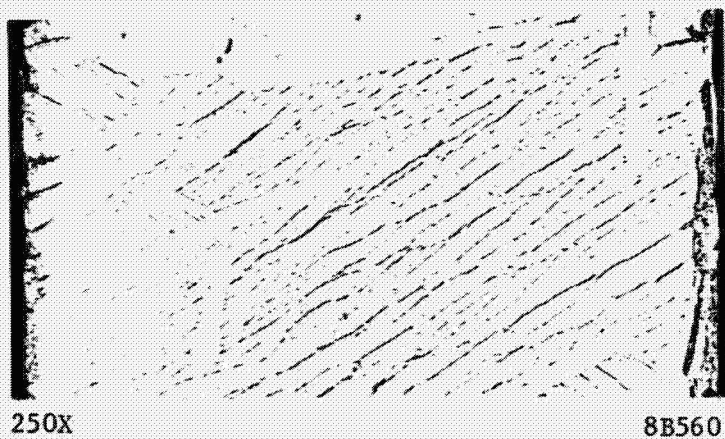


FIGURE 11. THE EFFECT OF HYDROGEN PRESSURE ON HYDRIDE-LAYER THICKNESS

All three samples were acicular Ti-50A and were reacted at 99 F.

However, one group of experimental runs was made to demonstrate the effect of temperature, time, and pressure on the titanium-hydrogen reaction. A summary of the results of this work is given in Table 6. Although the hydrogen pressure was varied from 15 to 1000 psia and time of exposure from 100 to 1000 hours, the hydrogen reactions apparently occurred in a random manner with no correlation observed between time and pressure. However, only those samples heated to 300 F reacted, no reaction occurred at 75 and 170 F regardless of pressure and time exposed. The relatively small number of samples which showed evidence of reaction was attributed to the fact that the reaction vessels were evacuated to no less than 10-microns pressure before introduction of hydrogen.

Surface Condition. One of the major factors in determining whether a reaction will occur between titanium and hydrogen is the cleanliness of the titanium surface. In these studies, immediately after abrasion of the titanium surface, an oxide film began to form. It was difficult to prevent this formation because after the sample was abraded, a short time interval elapsed before it was sealed into the reaction system and evacuated. This film was a critical factor in preventing the titanium-hydrogen reaction at atmospheric hydrogen pressures and near room temperature.

It was found that a 2-hour vacuum anneal at 1500 F apparently dissolved this oxide film and activated the surface so that a reaction occurred about half the time.

Table 7 presents a summary of a number of titanium-hydrogen experimental runs made at or slightly above room temperatures and at hydrogen pressures from atmospheric to 1000 psig. Various dry abrasion, rinsing (in cp acetone and distilled water), and vacuum annealing combinations were used to effect a clean surface and thus induce a hydrogen reaction.

It can be seen from these data that at hydrogen pressures up to 20 psig, vacuum annealing was necessary for a hydrogen reaction to take place. However, reaction was not always observed after this surface treatment. For 100 percent reaction, in addition to the abrading, rinsing, and annealing, a titanium foil getter had to be vacuum annealed with the sample.

A definite correlation between the amount of titanium foil included in the reaction vessel and both the hydrogen absorbed by the sample and the thickness of the hydride layer produced was observed. These correlations are given in Table 8. The effect of one run using nickel foil is also shown. It did not appear to be as effective a getter as titanium foil. Apparently the foil gettered any impurities dislodged from the glass, thus improving the vacuum, and also gettered any impurity from the hydrogen gas which may not have been removed by the cold trap (see the section on Hydrogen Purity).

The data in Table 7 also show that abrading, rinsing, and vacuum annealing, with or without foil, will produce a titanium-hydrogen reaction at hydrogen pressures above 20 psig. However, at the higher pressures, vacuum annealing was not an essential part of the surface cleaning procedure. Only abrasion was required.

TABLE 6. SUMMARY OF THE RESULTS OF EXPERIMENTS TO  
SHOW THE EFFECT OF TEMPERATURE, PRESSURE,  
AND TIME ON THE TITANIUM-HYDROGEN REACTION

Temperature, F	Time, hours	Number of Samples Reacting at Indicated Pressure <sup>(a)</sup>		
		1000 psig	300 psig	15 psig
300	1000	0	1	2
	100	0	3	0
	20	1	0	0
	10	0	3	0
170	1000	0	0	0
	100	0	0	0
75	1000	0	0	0

(a) Three samples were exposed in each test.

TABLE 7. THE EFFECTS OF SURFACE CONDITION ON THE REACTION OF TITANIUM AND HYDROGEN NEAR ROOM TEMPERATURE

<u>Sample Treatment</u>	<u>No. of Samples Treated</u>	<u>No. of Samples Which Reacted with Hydrogen</u>	<u>Percent of Samples Reacting</u>
<u>Atmospheric to 20 psig H<sub>2</sub> Pressure</u>			
Abraded, rinsed	6	0	0
Abraded, rinsed, and vacuum annealed	5	2	40
Abraded, rinsed, and vacuum annealed with Ti foil	11	11	100
Abraded, rinsed, and vacuum annealed with Ni foil	2	2	100
<u>Pressure of 20 psig and Greater</u>			
Rinsed only	5	1 <sup>(b)</sup>	20
Abraded, rinsed	24	24	100
Abraded, rinsed, and vacuum annealed	2 <sup>(a)</sup>	2	100
Abraded, rinsed, and vacuum annealed with Ti foil	2	2	100

(a) One sample was annealed 13 hours at 1000 F.

(b) This was the sample of tubing.

Note: All samples were abraded with dry 240-grit silicon carbide paper and rinsed in cp acetone or distilled water. Annealing was done for 2 hours at 1500 F in vacuum. Foil was 2-mil Ti-65A.

TABLE 8. THE EFFECT OF SURFACE AREA OF TITANIUM FOIL  
ON THE MAGNITUDE OF THE TITANIUM-HYDROGEN  
REACTION AND ON THE HYDRIDE THICKNESS

Area of Sample <sup>(a)</sup> Plus Foil, in <sup>2</sup>	Hydrogen Absorbed in 1 Hour, ml	Average Thickness of Titanium Hydride, mils
48	22	0.34 to 0.64
27	16	0.33 to 0.54
17.5	9	0.21 to 0.34
6	0	None formed
16.5 <sup>(b)</sup>	5 <sup>(c)</sup>	0.0 to 0.25

(a) Surface area of samples was 6 in<sup>2</sup>.

(b) Nickel foil used.

(c) Absorbed in 1-1/2 hours.

Table 9 presents a portion of the data in Table 7 in more detail. It shows the results of several attempts at hydriding titanium at high pressures with no abrasion of the surface, only degreasing or rinsing. No hydride was found on four of the samples. A fifth, which had been oxidized prior to hydrogen exposure, showed slight hydriding on one end. This probably resulted from a scratch in the oxide coating which exposed a clean titanium surface.

The effect of the oxide film always present when titanium is exposed to air is shown in Table 10 and Figure 12. As little as one minute exposure to air after vacuum annealing is sufficient time to prevent a hydriding reaction from occurring at atmospheric hydrogen pressure near room temperature. At 300 psig hydrogen pressure, a 1-1/2 hour exposure interval to air resulted in a decrease of 33 ppm in hydrogen pick-up (54 to 21 ppm) of the titanium sample.

**Stress.** It was considered possible that during stressing the thin oxide layer always present on titanium samples would be cracked. If so, stressing in a hydrogen atmosphere would expose a clean surface for attack by the hydrogen and the hydriding reaction would occur without any prior surface treatment. Therefore, the effects of stress, both cyclic and static on the titanium-hydrogen reaction, were examined. Table 11 summarizes this work and shows clearly that stress had little, if any, effect in initiating a titanium-hydrogen reaction. Only one of 37 samples, a Ti-6Al-4V alloy, reacted. The appearance of this sample is shown in Figure 13.

Twenty-six experimental runs were made at atmospheric hydrogen pressure and from 80 to 250 F in the clean glass system where the samples were bent from maximum tension through maximum compression once a minute. Fifteen of these were used to determine if cyclic strain accelerated the hydriding reaction. These tests are presented in more detail in Table 12. Except in one case, cyclic strain did not appear to cause a reaction in samples not vacuum annealed prior to stressing. As discussed earlier, vacuum annealing will cause a reaction to proceed without the presence of strain. Even though several samples broke from fatigue, thus creating fresh fracture surfaces, only the sample shown in Figure 13 indicated any evidence of reaction.

After hydriding had been initiated, the stressing apparently aided the hydriding reaction by causing spalling to occur, thus exposing more clean surface for attack by the hydrogen. The pitting attack shown here is similar to that observed on the liquid hydrogen storage tank gas delivery tube and suggests that the temperature cycle imposed on the tank was a factor in the failure process.

Eleven of the twenty-six samples stressed in one atmosphere of hydrogen had been deliberately exposed to air for varying periods of time and temperature to produce oxide layers of varying thickness. It was thought that stressing would more readily crack a thicker oxide layer. The results of these studies are presented in more detail in Table 13. The samples having the thicker oxide layers, 75 to 149 microinches, showed

TABLE 9. THE REACTION OF HYDROGEN WITH UNABRADED TITANIUM  
SAMPLES AT GREATER THAN ATMOSPHERIC PRESSURE

Temp., F	Hydrogen Exposure		Increase in Hydrogen Content, ppm $\pm$ 1	Description of Results
	Pressure, psig	Time, hr		
75	1000	6-1/3	--	No hydride found.
99	1000	6	5	Ditto
99	300	30-1/2	3	"
137	300	7-1/2	--	"
99	300	2-1/3	--	Thinly hydrided under oxide coating on one end <sup>(a)</sup> .

(a) Sample had been oxidized 36 hours at 1150 F in air before exposure to hydrogen. Oxide thickness, 57 microinches.



TABLE 10. THE EFFECT OF TITANIUM SURFACE EXPOSURE TO AIR, AFTER ABRASION AND BEFORE HYDROGEN ADDITION, ON THE TITANIUM-HYDROGEN REACTION AT NEAR ROOM TEMPERATURE

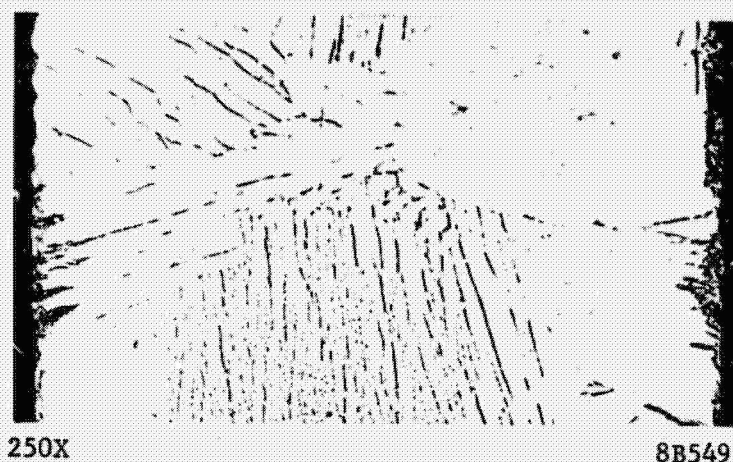
Sample Treatment	Time in Air	Description of Hydride
<u>Atmospheric Hydrogen Pressure</u>		
Abraded, rinsed, and vacuum annealed with Ti foil	1 min <sup>(a)</sup>	None formed.
<u>300 psig Hydrogen Pressure</u>		
Abraded, rinsed	5 min	Thin discontinuous hydride layer.
Ditto	15 min	Thin discontinuous hydride layer.
"(b)	15 min	Thin discontinuous hydride layer. Increase in hydrogen content $54 \pm 1$ ppm.
Abraded, rinsed	1 hr	Thin hydride in isolated areas.
Ditto	1-3/4 hr	Numerous small hydride areas. Increase in hydrogen content $21 \pm 1$ ppm.
Abraded, rinsed	2 hr	Thin hydride in isolated areas. Less than 1-hour sample.
Ditto	4 hr	Isolated spots of hydride. Less than 2-hour sample.
"	24 hr	A few very small irregular spots of hydride. Increase in hydrogen content $21 \pm 1$ ppm.
"(b)	128 hr	No hydride found.

(a) Exposed to air 1 minute after vacuum annealing.

(b) Sample was 1/8-inch diameter x 2-inch cylinder. All others were sheet, 2 inches x 1/2 inch x 15 mil.

Note: Abrasion was produced by dry 240-grit silicon carbide paper; cp acetone was used for rinsing.

- (a) Exposed to air 5 minutes after abrading and before exposure to hydrogen.



- (b) Exposed to air 1 hour after abrading and before exposure to hydrogen.



- (c) Exposed to air 4 hours after abrading and before exposure to hydrogen.

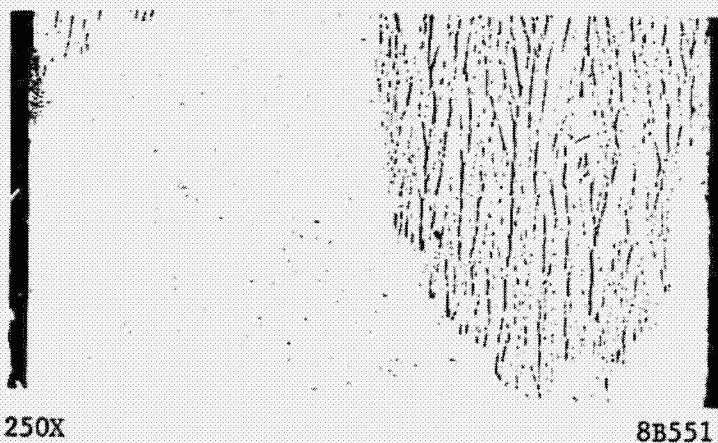


FIGURE 12. THE EFFECT OF EXPOSURE TO AIR AFTER ABRADING AND PRIOR TO EXPOSURE TO HYDROGEN

All three samples were acicular Ti-50A and were reacted with 300 psig hydrogen for 24 hours at 99 F.

TABLE 11. THE EFFECT OF STRESS ON THE  
TITANIUM-HYDROGEN REACTION

<u>Number of</u> <u>Samples Treated</u>	<u>Number of</u> <u>Samples Reacted</u>	<u>Percent of</u> <u>Samples Reacted</u>
<u>Cyclic, at 300 F and 300 psig Hydrogen Pressure</u>		
3	0	0
<u>Cyclic, at 80 to 250 F and</u> <u>Atmospheric Hydrogen Pressure</u>		
26(a)	1	~4
<u>Static, at 99 F and 300 psig Hydrogen Pressure</u>		
3	0	0
<u>Static, at 300 F and 300 psig Hydrogen Pressure</u>		
5	0	0

- (a) Three samples included in this summary were Ti-6Al-4V, one of which was the only stressed sample to react.



FIGURE 13. ACICULAR Ti-6Al-4V SHOWING RESULT OF HYDRIDING UNDER STRESS FOR 138 HOURS AT 80 F

Pitting occurred as a result of swelling of hydride.

Note: Smooth holes at one end were used to secure sample in holder.

TABLE 12. THE EFFECT OF CYCLIC STRAIN ON THE  
TITANIUM-HYDROGEN REACTION AT 80 TO  
250 F AND ATMOSPHERIC HYDROGEN PRESSURE

No. of Samples	Maximum Outer Fiber Strain, percent	Test Temp., F	Sample Vacuum Annealed	Hydriding Observed
<u>Acicular Ti-50A</u>				
1	0.3	80	Yes	Yes
7	0.3	80	No	No
1	0.3	250	No	No
2	1.0	80	No	No
1	1.0	80 & 170 <sup>(a)</sup>	No	No
<u>Acicular Ti-6Al-4V</u>				
2	0.3	80	No	Yes (on one sample only)
1	1.0	80	No	No

(a) Sample first stressed 89 hours at 80 F, then an additional  
27 hours at 170 F.

TABLE 13. THE EFFECT OF OXIDE FILM THICKNESS ON THE  
HYDRIDING OF CYCLIC STRESSED TITANIUM SAMPLES  
AT ATMOSPHERIC HYDROGEN PRESSURE

Oxide Film Thickness, $\mu$ in.	Maximum Outer Fiber Strain, percent	Test Temp., F	Hydriding Observed
<u>Acicular Ti-50A</u>			
15	0.3	80	No
22	0.3	80	No
28	0.3	80	No
75	0.3	80	No
20	0.3	140	No
75	0.3	80 & 140 <sup>(a)</sup>	No
57	1.0	80 & 140 <sup>(a)</sup>	No
75	1.0	80 & 140 <sup>(a)</sup>	No
149	1.0	80 & 140 <sup>(a)</sup>	No
<u>Equiaxed Ti-50A</u>			
12	0.3	80 & 140 <sup>(a)</sup>	No
11	1.0	80	No

(a) Samples stressed for varying times at 80 F before increasing temperature to 140 F.

a definite cracking of the gray-white outer layer under the effect of strain but no rupture of the inner bronze-colored oxide layer was noted. The outer layer did not crack on layers less than 75 microinches in thickness. No hydriding occurred with any sample.

Cyclic or static stress at 300 F in 300 psig of hydrogen initiated no hydriding reaction in the eight samples treated. The test conditions for these studies are shown in Table 14. In view of what has been discussed concerning the necessity for a clean surface before a hydriding reaction could be initiated (see section on surface condition), the failure of this series to react can easily be explained. A 1/2- to 3/4-hour time interval in air after abrading and before evacuation was necessary to secure the sample in its holder, seal the autoclave, and attach the assembly to the vacuum line. The best vacuum obtainable in the system was only 2 to 4 microns of mercury so that the residual contamination before the introduction of hydrogen was greater than that used to study the effects of pressure. This factor plus the oxide film formed during the exposure to air after abrading apparently prohibited the reaction.

As shown in Table 11 and in more detail in Table 15, no hydrogen reaction occurred in the statically stressed samples that were exposed to 300 psig hydrogen pressure at near room temperature without abrasion before exposure. Those that had been abraded before exposure to hydrogen showed the usual thin discontinuous hydride layer. However, this hydride was not concentrated in the stressed area but rather near the ends of the samples at locations that may have been galled during pre-bending. A hydrided area is shown in Figure 14. As will be discussed later, this is attributed to the effects of galling on the reaction.

In general, reactivity of the titanium with hydrogen under stress showed no increase under conditions when reaction normally occurred, nor was reactivity induced under conditions which did not lead to reaction in unstressed samples.

Galling. Galling, as the term is used in this work, refers to the rubbing or scratching of the titanium sample with another metallic substance or with a second sample of titanium. The term abrasion is used to describe the cleaning or roughening of the surface of the sample with an abrasive paper.

An intensive study was made of the effect of galling on the titanium-hydrogen reaction at 300 psig pressure of hydrogen near room temperature. Data were also obtained at atmospheric hydrogen pressure and at temperatures up to 300 F. The results of these investigations are summarized in Table 16. It is apparent from these data that all the metallic substances used as galling material caused a titanium-hydrogen reaction to occur at some time, depending on surface treatment before and after galling and the hydrogen pressure. It was necessary to vacuum anneal the sample after galling to produce a hydriding reaction at atmospheric pressure, but reaction occurred predominantly at the galled region. No foil getter

TABLE 14. SUMMARY OF DATA ON STRESSED (CYCLIC AND STATIC)  
TITANIUM SAMPLES AT 300 F IN 300 PSIG HYDROGEN

Time, hr	Stress <sup>(a)</sup> psi	Permanent Elongation in 1", percent	Hydriding Observed	Remarks
6	21,600	0.0	No	Held under constant load.
6	32,400	2.0	No	Held under constant load.
6	980 32,400	2.3	No	Cycled every 15 minutes between the low and high stress.
6	32,400	0.0	No	Oxidized 45 minutes at 1300 F in air before test.
6	32,400 to 38,300	<3.0	No	Same sample as above test; load progressively increased <sup>(b)</sup> . De- greased only; analysis after run, 56 ppm hydrogen.
6	39,000 <sup>(a)</sup>	4.0	No	Sample abraded and evacuated overnight.
29	39,000 <sup>(a)</sup>	6.5	No	Sample abraded and evacuated 1 hour.
46	980 32,400	11.0	No	Cycled every 15 minutes between low and high stress.

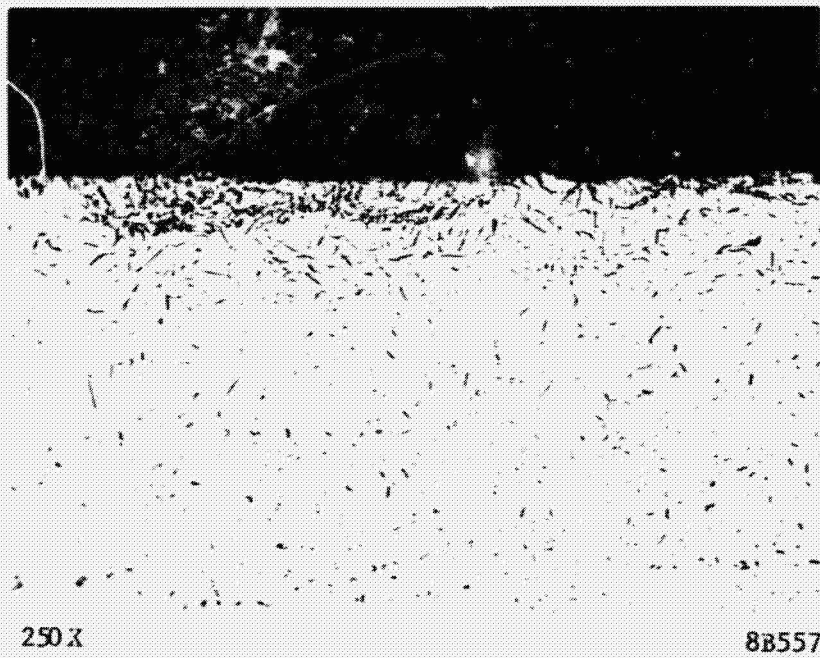
(a) These samples were heat treated to produce a coarse, acicular structure. All others had an equiaxed structure.

(b) Stress on this sample was successively 32,400 psi for 2.5 hours; 35,200 psi for 3.2 hours; and 38,300 psi for 0.3 hour.



TABLE 15. THE EFFECT OF STATIC STRESS ON THE TITANIUM-HYDROGEN REACTION AT 300 PSIG HYDROGEN PRESSURE, NEAR ROOM TEMPERATURE

Abraded Before Pressure Exposure	Structure	Description of Hydride
No	Acicular	No hydride found.
No	Cold rolled	No hydride found.
No	Equiaxed	No hydride found.
Yes	Acicular	Thin discontinuous hydride layer, not concentrated in strain area.
Yes	Cold rolled	Scattered spots of hydride, not concentrated in strain area. More appear to be near ends of sample.
Yes	Equiaxed	More hydride than in cold rolled sample, but not concentrated in strain area. More appear to be near ends.



250X

8B557

FIGURE 14. HYDRIDE ON EQUIAXED Ti-50A SAMPLE

Hydride found in area believed to be galled by dies during bending for static stress tests.

TABLE 16. THE EFFECT OF GALLING OF A CLEAN TITANIUM SURFACE ON THE TITANIUM-HYDROGEN REACTION

Pre-galling Sample Treatment	Galling Material	No. of Samples Treated	No. of Samples Reacted	Percent of Samples Reacted
<u>Room Temperature, Atmospheric Pressure</u>				
Abraded, rinsed, galled, vacuum annealed	Fe	5	2	40
	Ni	2	0	0
	Steel	1	1	100
Ditto	Ti	1	0	0
"	Wire brush	1	1	100
Abraded, rinsed, galled, vacuum annealed with Ti foil	Fe	2	2	100
Total		<u>12</u>	<u>6</u>	<u>50</u>
<u>300 F, Atmospheric Pressure</u>				
Abraded, rinsed, galled, vacuum annealed	Ni	2	2	100
	Fe	1	0	0
	Steel	1	0	0
Ditto	Wire brush	<u>1</u>	<u>0</u>	<u>0</u>
Total		<u>5</u>	<u>2</u>	<u>40</u>
<u>Room Temperature, 300 psig Hydrogen</u>				
Etched, galled, rinsed	Ti-50	11	8	73
Ditto	H-11	14	10	71
"	304 SS	2	1	50
"	C-3 tool	2	1	50
"	Fe	4	4	100
"	None	<u>2</u>	<u>0</u>	<u>0</u>
Total		<u>35</u>	<u>24</u>	<u>70</u>
<u>300 F, 300 psig Hydrogen</u>				
Etched, galled, annealed	Fe	1	0	0
Ditto	File	1	0	0
Degreased and galled only	Fe	2	1	50
	Ni	1	1	100
Ditto	Wire brush	1	0	0
Etched, galled	Fe	2	1	50
Ditto	Ni	2	0	0
"	Wire brush	<u>1</u>	<u>0</u>	<u>0</u>
Total		<u>11</u>	<u>3</u>	<u>27</u>

was used during most of these tests. Reaction at atmosphere pressure was more frequently observed in tests at room temperature than in tests at 300 F. This is attributed to the small amount of contamination coming from the glass system during heating. At 300 psig, the titanium-hydrogen reaction occurred with only galling of the material, preceded by a light  $\text{HNO}_3$ -HF cleaning etch. In this case, also, reaction was more frequently observed at room temperature than at 300 F. Outgassing of the furnace unit enclosed in the reaction vessel was suspected.

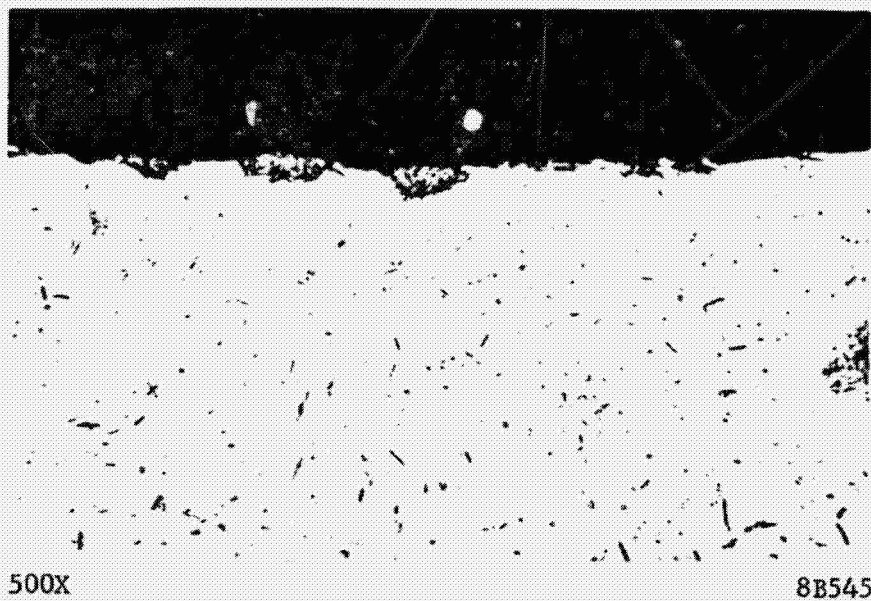
The exposure of the galled samples to air before the 300 psig hydrogen exposure resulted in a decrease in hydrogen reaction in the same manner as that for the abraded samples. After about 3 to 5 days in air following galling and before exposure to hydrogen, no reaction occurred in the laboratory studies.

As discussed in the introduction, it was observed that there was a considerable amount of hydride formation on the inside surface of the unalloyed tubing in the storage tanks which failed. This is shown in Figure 2. Galling of the inside of the tube by the mandrel over which it was fabricated was considered a likely explanation for this hydride film. Deliberate galling of the inside surface of another length of the same tubing with a steel rod before hydrogen exposure resulted in greatly increased hydriding reaction as compared to that observed in the "as-received" tube as shown in Figure 15. It also appears that the wire brushing of weld areas which was done before welding the connection fittings to the tube in the manufacture of the tanks might help explain the tendency for hydriding in these regions in the tanks.

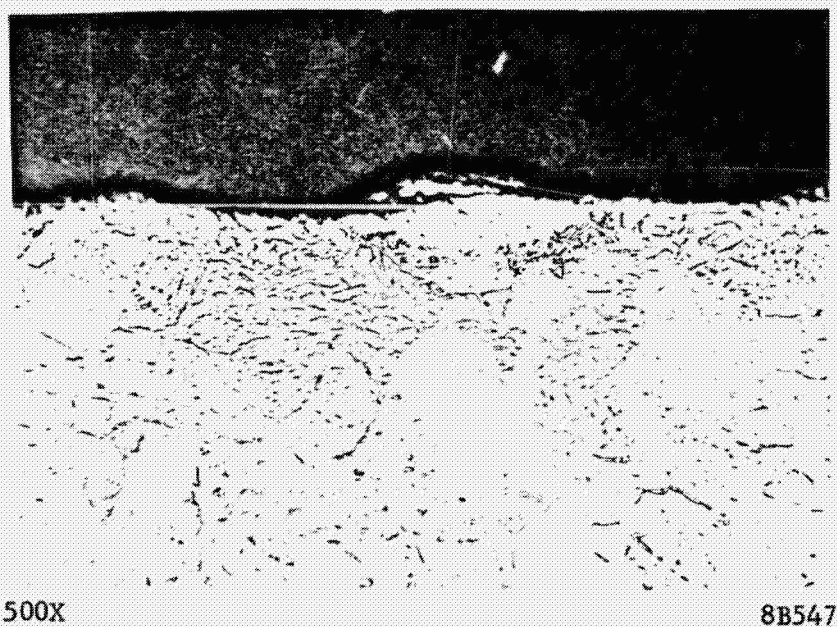
A further substantiation of the galling explanation for the initiation of the hydriding reaction in titanium came from the bending of samples for the static stress experiments. (Refer to the section on stress.) Instead of the concentration of the hydriding in the bent or stressed region, it occurred in the areas which were most likely galled during the pre-bending operation.

In an attempt to determine if contact of iron or nickel with no intentional galling on the surface of the titanium would initiate a titanium-hydrogen reaction, seven experimental runs were made, four with iron wire and three with nickel ribbon in contact with the titanium. Test samples were wrapped with iron or nickel. The wrapping material was then flattened on the surface of the test sample with a hammer. Test results are shown in Table 17. One sample bound with iron wire reacted slightly while two of those bound with nickel ribbon reacted, one extensively. The appearance of this last sample is shown in Figure 16. The reaction tended to occur where the nickel ribbon was in contact with the titanium. Since some galling of the titanium resulted from the hammering of the iron and nickel into contact with the sample, this may have produced the reaction rather than simple contact with the wrapping materials.

In nearly every case, samples which had been galled reacted only in or along the galled line or scratch. Even those samples which were abraded before galling and vacuum annealed after galling (for atmospheric hydrogen exposure) hydrided predominantly in the galled areas. Typical hydride formed under galled areas and under silicon-carbide abraded areas is illustrated in Figure 17.



(a) Reacted in the "as-received" condition with 300 psig hydrogen for 24 hours at 99 F



(b) Galled with H-11 steel before reacting with 300 psig hydrogen for 24 hours at 99 F

FIGURE 15. HYDRIDING OF THE INSIDE OF THE UNALLOYED TITANIUM TUBING

TABLE 17. THE EFFECT OF CONTACT OF TITANIUM WITH  
IRON WIRE AND NICKEL RIBBON ON THE  
TITANIUM-HYDROGEN REACTION

Sample Treatment	Temp., F	Hydrogen Pressure, psig	Hydriding Observed
<u>Iron Wire</u>			
Degreased only	300	300	No
Degreased and etched	300	300	No
Abraded, rinsed, vacuum annealed	200-300	Atmospheric	No
Ditto	80(a)	"	Yes
<u>Nickel Ribbon</u>			
Degreased only	300	300	Yes
Degreased and etched	300	300	No
Abraded, rinsed, vacuum annealed	300	Atmospheric	Yes

(a) The sample which did not react at 200-300 F  
was reannealed and used in this run.

FIGURE 16. MACROVIEW OF Ti-50A  
IN CONTACT WITH NICKEL  
RIBBON

Titanium hydride formed under turns of nickel ribbon during 22-hour exposure to one atmosphere of hydrogen at 300 F. Cracks indicating embrittlement of the titanium appeared when the sample was flattened slightly for photographing.



5X

Unetched

3H414

(a) Ti-50A galled  
with Ti-50A



(b) Ti-50A galled  
with H-11 steel



(c) Ti-50A abraded  
with 240-grit  
silicon carbide  
paper

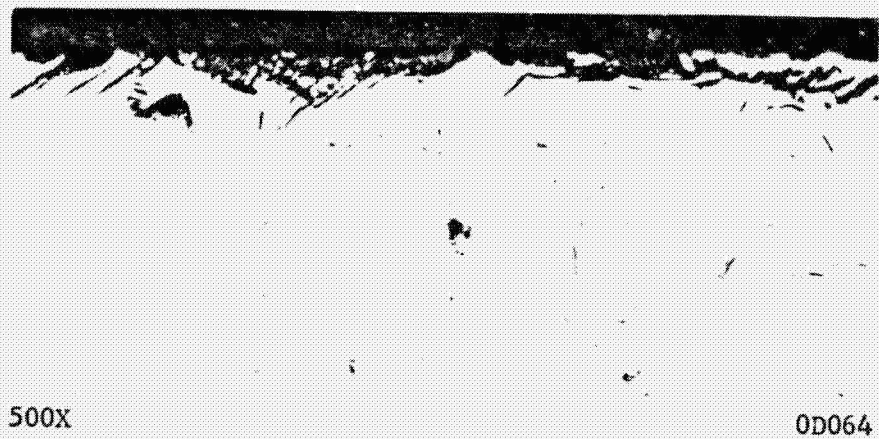


FIGURE 17. TYPICAL HYDRIDE FORMED UNDER GALLED  
AND ABRADED AREAS OF Ti-50A



The effect of three methods of galling, transverse reciprocating, longitudinal reciprocating, and by rotational galling on a lathe, on the reaction between hydrogen and titanium at 300 psig pressure is summarized in Table 18. Figure 18 illustrates the transverse and longitudinal galling procedures, while the lathe galling method is described in the section on experimental equipment and technique. It is apparent from Table 18 that a slight increase in hydrogen reaction results when the sample is galled transversely compared to a longitudinally galled sample. The quantity of hydride formed on a lathe-galled sample lies about midway between that of transverse and longitudinally galled ones. This difference in absorption with technique used is considerably larger when the sample is contaminated with oil during galling. (Refer to Tables 18 and 19 and to the section on contaminants.)

Studies of wear of metals in sliding contact have shown that transfer of metal tends to occur from the member having the larger area of contact to that having the smaller. Metal transfer was, therefore, from the titanium sample to the material in the stationary tool holder of the lathe, or to the transverse galled sample and away from the longitudinal galled sample. As shown in Table 18, the direction of metal transfer appears to have some effect on the hydriding reaction.

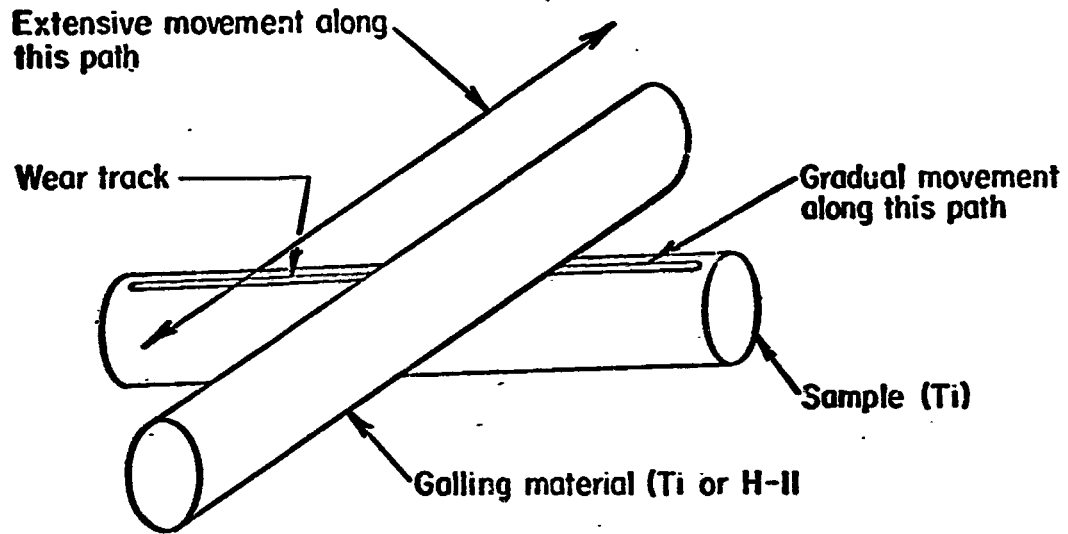
In these studies, transverse and longitudinal galling operations were done by hand, and the load applied could not be accurately maintained on each sample. From the lathe galling data in Table 18, it is apparent that the galling load affects the amount of hydrogen reaction. It was decided after this series of experimental runs that there was little to gain by hand galling, either transversely or longitudinally, over that by the lathe. In the lathe operation, the sample was galled evenly end to end with the same load and in the same time period, and the resultant galling could not be influenced by the operator.

**Contamination.** Ti-50A samples were galled with a number of materials after contamination the surface with oil. Iron, nickel, H-11 steel, 304 stainless steel, C-3 tool bit, and titanium were chosen as galling materials as they are commonly found in industrial use and are quite likely to come in contact with the titanium while contaminated with oil during processing. An indication of the amount of hydride formed on the titanium as affected by oil contamination is given in Table 19. Samples galled or abraded in a similar manner and exposed to air for about the same length of time after galling or abrading before hydrogen exposure showed little difference in hydrogen absorption resulting from the material used in galling. Contamination of the samples with oil before galling resulted in considerably more reaction than was observed with samples which were not so treated.

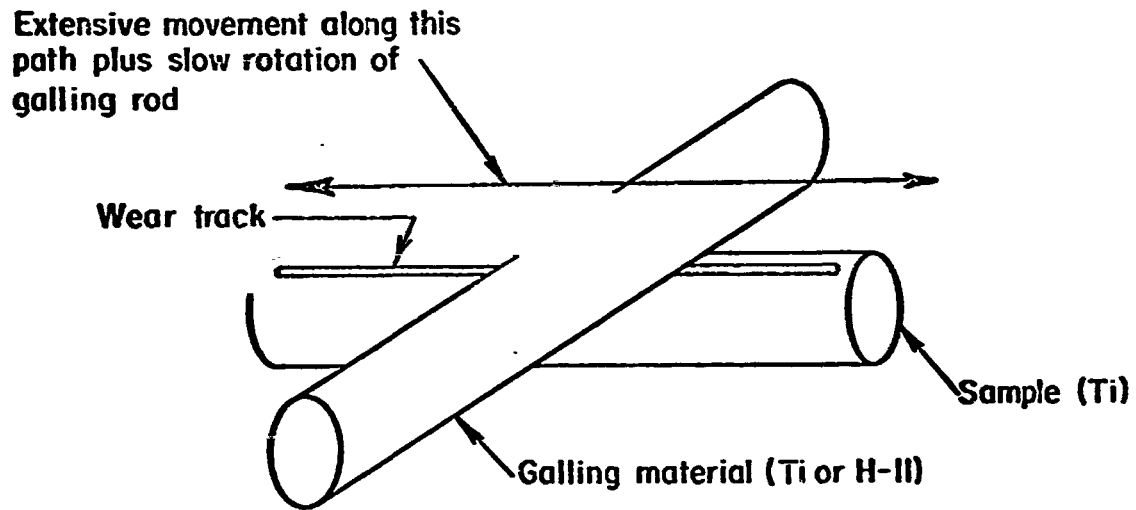
In Table 19, samples must be compared which have had periods in air of nearly equal length after galling or abrasion and before hydrogen exposure. This is necessitated by the dependence of the quantity of hydrogen absorbed on the length of pre-exposure to air.

TABLE 18. HYDROGEN ABSORPTION AT 300 PSIG  
AS A FUNCTION OF GALLING TECHNIQUE

Galling Material	Galling Direction	Increase in Hydrogen Content, ppm $\pm$ 1
H-11	Transverse	18
"	"	8
"	"	<u>6</u>
	Average	11
H-11	Longitudinal	9
"	"	4
"	"	<u>0</u>
	Average	4
H-11	Lathe	11
"	"	<u>5</u>
	Average	8
Oiled	Transverse	147
H-11	Longitudinal	73
Oiled	In lathe,	97
Ti-50	32-oz. load	
Ditto	In lathe,	37
	8-oz. load	



a. Transverse galling



b. Longitudinal galling

FIGURE 18. TWO PROCEDURES USED TO GALL TITANIUM SAMPLES

TABLE 19. EFFECT OF GALLING MATERIAL, BOTH CLEAN AND OILY, ON THE HYDRIDING REACTION OF TITANIUM SAMPLES AT 300 PSIG AND NEAR ROOM TEMPERATURE

Method of Galling or Abrasion	Galling or Abrasive Material	Contaminant	Time in Air After Galling or Abrasion and Before Hydrogen Exposure	Increase in Hydrogen Content, ppm $\pm$ 1
Transverse rubbing	Ti-50	Oil	~ 95 min.	77
	H-11 steel	"	"	87
bitto	Ti-50	"	~ 73 hr.	11
"	H-11 steel	"	"	16
"	SiC paper	"	"	12
"	Ti-50	None	~ 20 hr.	4
"	H-11 steel	"	"	5
"	Ti-50	"	~ 128 hr.	1
"	H-11 steel	"	"	1
Galled in lathe, 8-oz. load	Ti-50	Oil	~ 80 min.	34
	H-11 steel	"	"	36
Ditto	SiC paper	"	"	65
"	Ti-50	None	~ 2 hr.	0
"	H-11 steel	"	"	8
"	304 SS	"	"	0
"	C-3 tool material	"	"	-1
"	SiC paper	"	"	20
Galled in lathe, 32-oz. load	Ti-50	Oil	~ 1 to 4-1/2 hr.	97
	H-11 steel	"	"	64
Ditto	304 SS	"	"	64
"	C-3 tool material	"	"	130
"	SiC paper	"	"	64

It has been shown that a contaminated surface aided the titanium-hydrogen reaction of galled or abraded samples at 300 psig hydrogen pressure. The effects of a number of contaminants on hydriding were examined including oil, graphite,  $\text{Fe}_2\text{O}_3$  powder,  $\text{NaCl}$ ,  $\text{MoS}_2$  + graphite,  $\text{SiC}$  powder,  $\text{Al}_2\text{O}_3$  cloth, dirt from a concrete floor, and natural oils from the fingers. A reaction with hydrogen took place with the use of every contaminant provided that the surface was galled or abraded while in contact with the contaminant. An oiled or graphite impregnated surface failed to react with hydrogen when not galled or abraded. When comparison was possible, those samples contaminated with oil during galling showed an increase in hydrogen absorption over those galled under clean conditions as shown in Table 20.

Exposure of samples, galled in the presence of a contaminant, to air after galling tended to retard the hydriding reaction at 300 psig in somewhat the same way as air exposure retarded hydriding of samples abraded in a clean condition. This is shown in the following tabulation for oiled samples:

<u>Time in Air After Galling</u>	<u>Increase in Hydrogen Content, ppm <math>\pm</math> 1</u>
87 min.	52
143 min.	42
148 hr.	10

As shown above, an increase in hydrogen content of 10 ppm was measured when oily galled samples were exposed to hydrogen at 300 psig after almost one week in air. It should be recalled that hydriding in hydrogen at one atmosphere pressure can be completely prevented by a one-minute air exposure of vacuum annealed titanium, and in hydrogen exposure at 300 psig, by a period between one and five days air exposure. After galling, a light rinse with cp acetone was used to eliminate gross oil residues. A thin film of oil always remained on each sample, however. Apparently, this thin oily film acts as a protective film over the galled or abraded surfaces, thus tending to prevent the oxidation of the sample by air. The oxide layer which normally forms rapidly after abrasion or galling and in time prevents a hydrogen reaction is thus eliminated or slowed in formation allowing hydriding to take place.

A maximum of one week exposure in air after galling in the presence of oil and hydrogen exposure was investigated in this work. It is believed that contaminated titanium surfaces may retain the ability to react with hydrogen to at least some extent for much longer periods of time especially if the contaminated surface is one which is difficult to clean. This appears to be the case with the tubing on the storage tank described in the Introduction where hydriding was found on the inside surfaces of the tubing. It was not known how long this tubing had been exposed to air after fabrication and probable galling in the tube drawing process before hydrogen exposure. However, reaction was observed in samples of this tubing exposed to hydrogen at 300 psig after several months' exposure to air in the laboratory.

TABLE 20. A COMPARISON OF HYDROGEN ABSORPTION OF CLEAN GALLED OR ABRADED TITANIUM SAMPLES AND THOSE CONTAMINATED WITH OILY MATERIAL DURING GALLING AND ABRADING

Galling or Abrasion Material	Contamination	Increase in Hydrogen Content, ppm $\pm$ 1
Ti-50%	None	4
"	Oil	11(a)
"	None	7
"	Oil	77
"	None	11
"	Fingerprints	84
Al <sub>2</sub> O <sub>3</sub> paper	None	5
"	Oil	47
SiC paper	None	31
"	Oil	65

(a) This oiled sample was exposed to air 73 hours after galling while the clean sample was exposed to air for only 20 hours. All other comparisons are based on samples having similar air exposure time after galling, about 1/2 to 2 hours.

Material Composition. The reaction between unalloyed titanium (Ti-50A) and hydrogen has been described in previous sections of this report. In addition, several titanium alloys were exposed to hydrogen in order to determine if alloy composition affected the reaction. These included Ti-75A (a higher interstitial grade of unalloyed titanium), Ti-5Al-2.5Sn, Ti-6Al-4V, and Ti-13V-11Cr-3Al. A length of unalloyed titanium tubing from the lot used to fabricate the tank described in the Introduction was also examined.

Hydrogen diffusion is considerably more rapid in beta than in alpha titanium. Consequently, in the hydrogen reactions with unalloyed titanium and Ti-5Al-2.5Sn, a hydride formed on the surface of the samples and could be detected microscopically. In the Ti-13V-11Cr-3Al and Ti-6Al-4V alloys, no hydride layer was formed unless the concentration in the metal reached about 500 ppm. Thus, vacuum fusion hydrogen analysis was necessary to detect a hydrogen reaction in these alloys.

A summary of hydrogen reactions with the titanium alloys is given in Table 21. As the Ti-75A alloy showed no significant difference in reactivity over that of Ti-50A, it does not appear in this table and will not be discussed further.

Based on data given in Table 21, it generally appears that the Ti-5Al-2.5Sn and Ti-13V-11Cr-3Al alloys were the most reactive of the materials examined. The least reactive was the Ti-6Al-4V alloy. The Ti-13V-11Cr-3Al alloy, used only in three experimental runs, showed a violent, catastrophic reaction, as shown in Figure 19, in one sample and a large amount of hydrogen pick-up in a second sample. No runs were made at 300 psig hydrogen pressure with this alloy. Table 22 compares the quantity of hydrogen reacted with Ti-50A, Ti-5Al-2.5Sn, and Ti-6Al-4V at 300 psig pressure. It can be seen that here, as in Table 21, Ti-5Al-2.5Sn is the most reactive and Ti-6Al-4V the least.

The tubing reacted with 300 psig hydrogen pressure in the "as-received" condition (degassed only) as shown in Figure 15. This was the only sample in this study that reacted with hydrogen without some form of surface treatment or preparation prior to exposure to hydrogen. It also reacted, and to a greater extent, after galling with H-11 steel at room temperature and at 400 F.

Material Structure. Three types of microstructure produced in the Ti-50A titanium study were examined in some detail. These were coarse acicular, equiaxed, and cold rolled. The treatments used to produce these structures and typical microstructures are presented in the Materials section.

Table 23 shows the effect of microstructure along with air exposure on the titanium-hydrogen reaction near room temperature and 300 psig hydrogen pressure. The coarse acicular structure proved to be the most reactive with hydrogen and least affected by exposure to air after abrasion. There was little difference in the reactivity of the cold-rolled and equiaxed material except that a slight reaction with hydrogen had still occurred after 4 hours of exposure to air with the cold-rolled material but not with the equiaxed material.

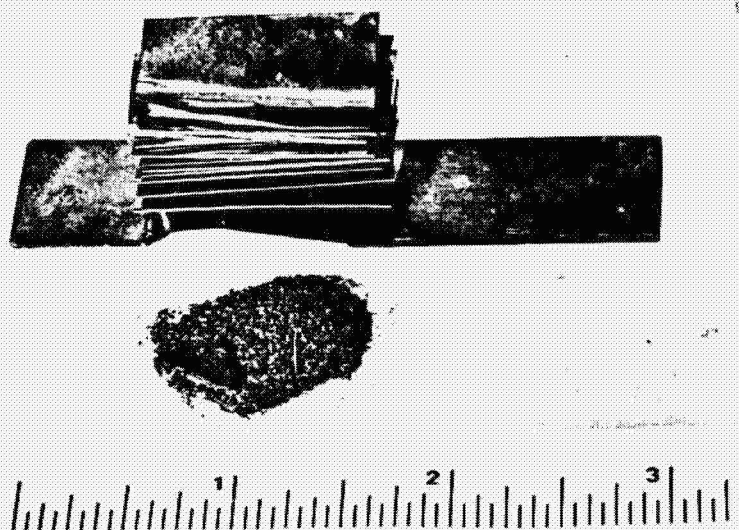
TABLE 21. SUMMARY OF THE EFFECT OF HYDROGEN NEAR ROOM TEMPERATURE ON TITANIUM ALLOYS

Alloy	Pretreatment	No. of Samples Treated	No. of Samples Reacted	Percent of Samples Reacted
<u>Atmospheric Hydrogen Pressure</u>				
Ti-6Al-4V	Abraded, vacuum annealed, 2 with Ti foil	4	2 <sup>(a)</sup>	50
Ti-5Al-2.5Sn	Abraded, vacuum annealed with foil	3	2	67
Ti-13V-11Cr-3Al	Abraded, vacuum annealed with foil	3	2	67
Ti-50A	Abraded, vacuum annealed with and without foil	24	15	63
<u>300 psig Hydrogen Pressure</u>				
Ti-5Al-2.5Sn	Galled or abraded and rinsed	16	15	94
Ti-6Al-4V	Galled or abraded and rinsed	10	6	60
Ti-50A	Galled or abraded and rinsed	33	24	73
<u>Cyclic Stressed, Atmospheric Hydrogen Pressure</u>				
Ti-6Al-4V	Samples not vacuum annealed. Foil annealed in one run, none used in other run.	2	1	50
<u>Static Stress, 300 psig Hydrogen Pressure</u>				
Ti-6Al-4V	Abraded, rinsed	1	1 <sup>(b)</sup>	100

(a) One sample reacted which had no Ti foil in system as pretreatment, and one reacted which did contain the foil.

(b) Analysis showed 22 ppm hydrogen above base analysis; however, hydrogen was not concentrated in stressed area.





1.2X

32400

FIGURE 19. MATERIAL REMAINING IN REACTION TUBE AFTER Ti-13V-11Cr-3Al REACTED CATASTROPHICALLY WITH HYDROGEN

Ti-13V-11Cr-3Al sample is on the left. Ti-5Al-2.5Sn sample is on the right with accordian-pleated foil getter on top of both samples. All but 5/8 inch of the original 1-1/2 inch of the Ti-13V-11Cr-3Al sample disintegrated into the powder at front center. The Ti-5Al-2.5Sn sample showed slight hydriding. The foil getter was heavily hydrided.

TABLE 22. A COMPARISON OF THE QUANTITY OF  
HYDROGEN REACTED WITH TITANIUM  
AND THAT REACTED WITH ITS ALLOYS  
AT 300 PSIG

Sample Material	Galling Material	Increase in Hydrogen Content, ppm $\pm$ 1
Ti-50A	Oiled Ti-50A	47
	Oiled H-11 steel	34
Ti-5Al-2.5Sn	Oiled Ti-5Al-2.5Sn	50
	Oiled H-11 steel	51
Ti-6Al-4V	Oiled Ti-6Al-4V	3
	Oiled H-11 steel	11

TABLE 23. SUMMARY OF THE EFFECT OF TITANIUM MICROSTRUCTURE AND THE EFFECT OF SAMPLE EXPOSURE TO AIR ON THE TITANIUM-HYDROGEN REACTION

Time in Air	Description of Hydride
<u>Coarse Acicular Ti-50A</u>	
5 min.	Thin discontinuous hydride layer.
15 min.	Thin discontinuous hydride layer.
1 hr.	Thin layer in isolated areas.
2 hr.	Thin layer in isolated areas (less than after 1 hr.).
4 hr.	Isolated spots of hydride.
<u>Cold Rolled Ti-50A</u>	
5 min.	Thin hydride layer in isolated spots.
15 min.	Thin hydride layer in isolated spots (less than 5 min. sample).
1 hr.	A few isolated spots of hydride.
2 hr.	A few isolated spots of hydride (less than 1 hr. sample).
4 hr.	A few isolated spots of hydride (less than 2 hr. sample).
<u>Equiaxed Ti-50A</u>	
5 min.	Thin discontinuous hydride layer.
15 min.	Thin hydride layer in isolated areas.
1 hr.	Thin hydride layer in isolated areas (less than 15 min. sample).
2 hr.	Isolated spots of hydride.
4 hr.	No hydride found.

Note: All samples exposed to 300 psig hydrogen at 99 F.

Table 24 shows the effect of the microstructure on the hydride thickness of three annealed Ti-50A samples reacted at 300 F with 300 psig hydrogen pressure. Here, as in the results shown in Table 23, the coarse acicular structure proved to be the most reactive as indicated by the greater thickness of the hydride layer after exposure for either 10 or 100 hours. The equiaxed and fine acicular structures showed little difference in activity.

The greater activity of the coarse acicular structure is also shown in Table 15. In this case, stress was applied to acicular, cold rolled, and equiaxed titanium under 300 psig hydrogen pressure. A thin, discontinuous hydride layer was found over the entire surface of the sample having an acicular structure and only in scattered spots on the equiaxed and cold rolled material.

A reasonably consistent microstructural trend was observed in the entire experimental program. Unalloyed titanium samples having a coarse acicular microstructure, developed by slow cooling after heating into the beta region, showed a greater tendency for the hydriding reaction to occur and thicker hydride scales were formed. Hydride formed on titanium having the coarse acicular structure usually was more or less uneven with rather deep penetration along the crystal faces, whereas the hydride formed on equiaxed material was usually quite uniform. This is shown in Figure 20.

Much of the hydriding in the liquid hydrogen tanks and tubing connections described in the Introduction was in the vicinity of welds. The microstructure of titanium which has been subjected to heating and cooling during the welding process is acicular, and depending on cooling rate, can be quite coarse. This may account in part for the observed tendency for hydriding to concentrate in weld regions.

Time. Three aspects of time were considered in this work:

- (1) time in air after abrasion or galling and before hydrogen exposure,
- (2) length of time to evacuate the system before the addition of hydrogen, and
- (3) the length of time of the hydrogen exposure.

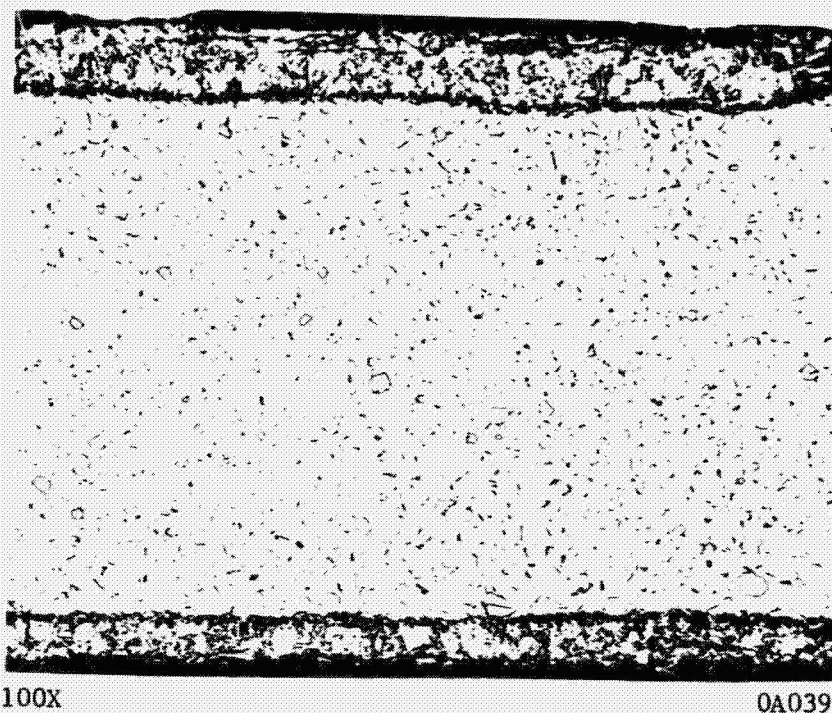
The correlation between time in air after abrasion or galling and the degree of reaction observed on exposure to hydrogen has already been discussed in the sections on galling and surface condition.

Table 25 shows a comparison of the effect of evacuation time before introduction of hydrogen to the system on the hydrogen reaction. Little, if any, difference was noted in the reaction of Ti-50A whether evacuated 4 or 64 hours although a slight increase in hydrogen reaction with evacuation time was noted for Ti-5Al-2.5Sn.

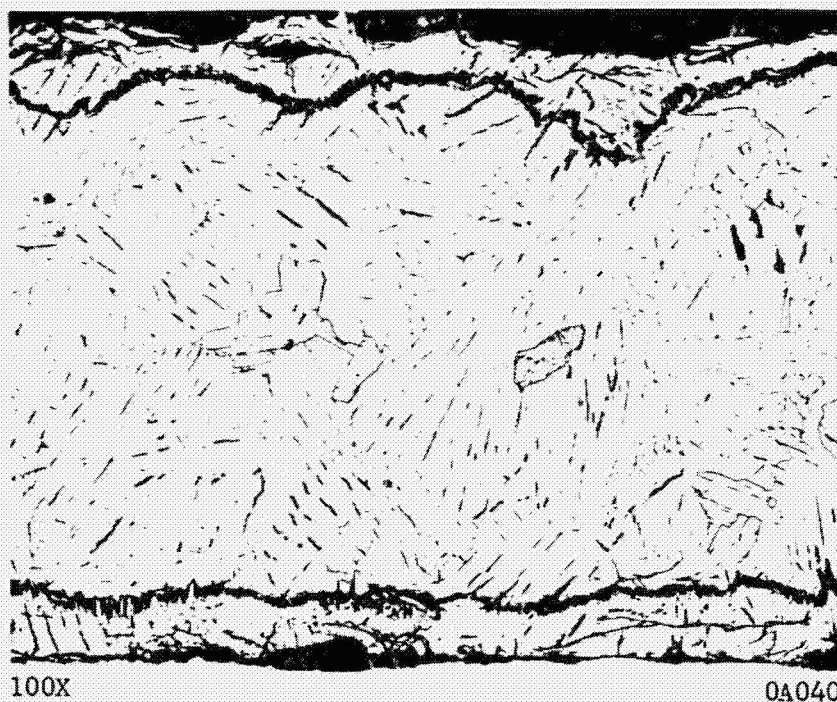
The correlation between length of hydrogen exposure and amount of hydrogen reaction was examined only briefly. In a simultaneous study of the effects of time, temperature, and pressure on the reaction, the hydride layer thickness was greater after 100 hours at 300 psig and 300 F than after 10 hours' exposure as shown in Table 24.

**TABLE 24. EFFECT OF TITANIUM MICROSTRUCTURE ON THE HYDRIDE LAYER THICKNESS OF SAMPLES REACTED AT 300 F AND 300 PSIG HYDROGEN PRESSURE**

Time of Exposure, hr	Condition	Thickness of Hydride Layer, Average (mils)
10	Fine grained equiaxed	2.5
"	Coarse acicular	3.5
"	Fine acicular	2.8
100	Fine grained equiaxed	3.0
"	Coarse acicular	4.5
"	Fine acicular	2.8



(a) Hydride formed on equiaxed Ti-50A after a 10-hour exposure to hydrogen at 300 psig and 300 F



(b) Hydride formed on coarse acicular Ti-50A after a 10-hour exposure to hydrogen at 300 psig and 300 F

FIGURE 20. A COMPARISON OF HYDRIDE FORMED ON Ti-50A HAVING EQUIAXED AND ACICULAR MICROSTRUCTURE

TABLE 25. A COMPARISON OF HYDROGEN ABSORPTION  
WITH LENGTH OF EVACUATION TIME

Sample Material	Galling Material	Increase in Hydrogen Content, ppm $\pm 1$ (a)	
		Evacuated 4 hr	Evacuated 64 hr
Ti-50A	Ti-50A	0	0
"	H-11 steel	11	5
"	304 SS	0	-2
"	C-3 tool	1	-5
"	SiC	11	29
Ti-5Al-2.5Sn	Ti-5Al-2.5Sn	2	3
"	H-11 steel	3	14
"	304 SS	3	3
"	C-3 tool	5	10
"	SiC	4	20

(a) Samples exposed 64 hours at 300 psig.

In work at atmospheric hydrogen pressure, a manometer connected in the system made it possible to determine if a hydrogen reaction was taking place. The reaction normally began immediately and was usually allowed to continue overnight, 16 to 18 hours. After this time, the reaction had usually stopped or was proceeding very slowly due to the decrease in hydrogen pressure which accompanied reaction. No rate measurements were made. In this work, it was found that if a hydrogen reaction failed to begin almost immediately after the exposure to hydrogen, no reaction would take place regardless of the length of the exposure time.

With runs made at high pressures, the drop in pressure which resulted when the samples did hydride was not of a sufficient magnitude to be read from the pressure gage. Because of this, most experimental runs made at high pressure were allowed to react for about 64 hours to insure that ample time was provided for the reaction to occur.

Galling During Hydrogen Exposure. Several experimental runs were made using the apparatus shown in Figure 8 where galling of the sample could be accomplished while in a moderate pressure of hydrogen.

Metallographic examination showed hydriding occurred on Ti-50A samples after only 30 minutes exposure to 50 psig hydrogen pressure during galling. Hydride was found along the sides of the notches worn into the stationary sample as shown in Figure 21 as well as along the galled area of the moving sample. Galling in a hydrogen atmosphere was able to initiate a reaction on samples having no prior surface treatment. A summary of all the experimental work completed on galling in hydrogen at 50 psig is shown in Table 26. Changes in weight were used to determine the amount of reaction. Weight changes during galling in a hydrogen atmosphere were compared with samples galled for identical time periods in air at atmospheric pressure. It was assumed that as hydride formed, it would be rapidly worn away during galling such that the amount of reaction would be directly related to weight loss. Measurements were made of the depth of the notch worn into several of the stationary samples (Sample B) to determine whether notch depth correlated with the loss in weight. As shown in the following tabulation, a fairly good correlation existed:

<u>Depth of Notch,</u> <u>mils</u>	<u>Weight Loss,</u> <u>mg</u>
5.0	0.8
7.5	0.8
10.0	2.7
15.0	2.8
17.5	3.2
30.0	11.3
65.0	46.6

In a few cases, samples were also analyzed to determine hydrogen pick-up after hydrogen exposure during galling.

As shown in Table 26, the Ti-6Al-4V alloy was most reactive, the Ti-5Al-2.5Sn samples were next in reactivity, and Ti-50A was least reactive. The presence of oil seemed to increase the amount of hydriding. Analyses





500X

6D531

FIGURE 21. HYDRIDE FORMED ON THE STATIONARY Ti-50A SAMPLE

The light band along the notch surface is hydride.

TABLE 26. SUMMARY OF THE RESULTS OF GALLING SAMPLES WHILE UNDER HYDROGEN PRESSURE<sup>(a)</sup>

Material		Exposure Time, min.	Atmos- phere	Sample Weight Loss, mg			Remarks
A	B			A	B	Total	
Ti-50A	Ti-50A	90	H <sub>2</sub>	1.1	7.3	8.4	Average of 3 samples. Sample B showed 8 ppm hydrogen increase.
Oiled Ti-50A	Ti-50A	90	H <sub>2</sub>	9.3	3.2	12.5	
H-11	Ti-50A	90	H <sub>2</sub>	2.0	11.3	13.3	
Ti-50A	Ti-50A	90	Air	2.7	2.5	5.2	
Ti-50A	Ti-50A	30	H <sub>2</sub>	1.1	1.7	2.8	Average of 3 samples.
Ti-50A	H-11	30	H <sub>2</sub>	1.4	--	--	
Ti-50A	Ti-50A	30	Air	1.9	0.3	2.2	Average of 5 samples.
Ti-5-2.5	Ti-5-2.5	90	H <sub>2</sub>	15.9	2.9	18.8	Average of 2 samples <sup>(b)</sup> .
Ti-5-2.5	Ti-5-2.5	90	Air	1.9	0.8	2.7	
Ti-6-4	Ti-6-4	90	H <sub>2</sub>	10.0	13.2	23.2	Average of 3 samples.
Oiled H-11	Ti-6-4	180	H <sub>2</sub>	10.4	46.6	57.0	Sample B showed 14 ppm hydrogen increase.
Ti-6-4	Ti-6-4	90	Air	1.6	0.8	2.4	

(a) Hydrogen pressure was 50 psig and temperature about 75 F. All samples etched in a solution of 67 parts H<sub>2</sub>O, 33 parts HNO<sub>3</sub>, and 3 parts HF before exposure to galling in hydrogen. Sample A was the moving sample; Sample B, the stationary one.

(b) One pair of samples was analyzed. Hydrogen increase was 14 ppm in Sample A and 8 ppm in Sample B.

showed a 14 ppm hydrogen content increase in the stationary sample of Ti-6Al-4V and an 8 ppm increase in similarly treated sample of Ti-50A. A pair of Ti-5Al-2.5Sn samples galled without oil present were also analyzed. The stationary sample picked up 8 ppm and the moveable sample 14 ppm. A considerable amount of powder material was present on the apparatus floor below the point of contact of samples galled in hydrogen. This material was presumed to be hydride.

There did not appear to be a consistent pattern in the amount of weight lost from the stationary and moveable samples. Sometimes one lost more weight and sometimes the other. Presumably, this difference is related in some way to the properties of the materials studied--probably to hardness and work hardening rate--but the test program was not sufficiently broad to demonstrate the origin of the variable weight loss pattern.

In spite of the inconsistencies in the test data, the experimental work showed that galling of titanium and its alloys while exposed to hydrogen at pressures as low as 50 psig will initiate a hydriding reaction in a relatively short time.

#### Prevention of Hydriding

It has been proved that titanium will hydride at near room temperature and atmospheric hydrogen pressure if a clean surface is exposed to clean hydrogen. At higher hydrogen pressures, a clean surface also reacts with hydrogen, but an oily galled or scratched surface is much more reactive.

In order to prevent hydriding from taking place, the titanium surfaces should be removed along with any oily contamination on the surface. Removal of the galled, oily contamination can be accomplished by degreasing with cp acetone and pickling the surface with a solution consisting of 67 parts H<sub>2</sub>O, 33 parts HNO<sub>3</sub>, and 3 parts HF.

The data shown in Table 27 illustrate the effects of pickling in retarding the hydriding of titanium. In each material, a 30-second pickle lowered the amount of hydrogen absorbed considerably. By pickling to remove about 2 mil of surface, hydriding was eliminated. No hydride was visible microscopically on any sample from which 2 mils had been removed by pickling. The small increase in hydrogen content above that of the base analyses of heavily pickled Ti-50A and Ti-5Al-2.5Sn samples is believed due to the hydrogen pick-up from the pickling solution.

The presence of an oxide layer on the surface of titanium was shown in the section on contamination to decrease hydriding. If exposed to air for a sufficient length of time, hydriding was considerably retarded. The time in air required to prevent a hydrogen reaction was found to be only about one minute after vacuum annealing and before exposure to atmospheric hydrogen pressure and approximately 5 to 6 days for samples exposed to 300 psig hydrogen pressure. The effectiveness of exposure to air is shown in Table 27 for material galled in the presence of oil. As shown by these data, some reaction still took place after 6 days exposure to air.

TABLE 27. SUMMARY OF RESULTS IN ATTEMPTS TO PREVENT THE TITANIUM-HYDROGEN REACTION

Alloy	Galling Material	Treatment Attempted to Prevent Hydriding	Increase in Hydrogen Content, ppm $\pm$ 1
Ti-50A	Oiled Ti-50A	None (control)	47 (Avg of 2)
"	Ditto	Pickled 30 seconds	13 (Avg of 2)
"	"	Pickled 2 mil off diameter	5 (Avg of 2)
"	"	Exposed to air 148 hr after galling and before H <sub>2</sub> exposure	10
"	"	Annealed 2 hr at 1100 F in argon	31
"	Clean Ti-50A	Ditto	9
"	Oiled Ti-50A	Cleaned thoroughly in cp acetone after galling	39 (Avg of 2)
Ti-5Al-2.5Sn	Oiled Ti-5Al-2.5Sn	None (control)	50 (Avg of 2)
"	Ditto	Pickled 30 seconds	22 (Avg of 2)
"	"	Pickled 2 mil off diameter	12 (Avg of 2)
"	"	Exposed to air 148 hr after galling and before H <sub>2</sub> exposure	20
"	"	Annealed 2 hr at 1100 F in argon	47
"	"	Cleaned thoroughly in cp acetone after galling	45 (Avg of 2)
Ti-6Al-4V	Oiled Ti-6Al-4V	None (control)	12 (Avg of 2)
"	Ditto	Pickled 30 seconds	0 (Avg of 2)
"	"	Pickled 2 mil off diameter	-5 (Avg of 2)
"	"	Exposed to air 148 hr after galling and before H <sub>2</sub> exposure	9
"	"	Annealed 2 hr at 1100 F in argon	52
"	"	Cleaned thoroughly in cp acetone after galling	5 (Avg of 2)

An alternate method of preventing a hydriding reaction of galled material was considered to be annealing to diffuse any metallic contamination from the surface into the alloy. To prevent oxidation from masking the effects of the diffusion treatment, samples were encapsulated and annealed in a 99.996 purity argon atmosphere. A 2-hour anneal at 1100 F was used. The results of these studies, as shown by the hydrogen content differences shown in Table 27, are difficult to interpret. Apparently, some increase in hydrogen content occurred during the argon anneal as a result of pick-up of hydrogen from the residual oil film. Unfortunately, analyses of these samples were not made after the argon anneal and before hydrogen exposure. Metallographic examination of the samples showed about the same amount of hydride to be present on the argon annealed Ti-50A and Ti-5Al-2.5Sn samples after hydrogen exposure as was present on the sample exposed after galling. The Ti-6Al-4V material was relatively free of hydride after both treatments. It is concluded, therefore, that the diffusion annealing treatment was of little value in preventing a hydrogen reaction.

Removal of the oily contamination after galling and before hydrogen exposure did not eliminate hydriding although it retarded it somewhat as shown in Table 27. In this case, complete removal of oily contamination was desired. This was accomplished by a rinse in cp acetone followed by a 5-minute acetone soak with agitation, then another acetone rinse. Cleaning is probably effective in retarding the reaction by restoring the surface oxidation rate to that which is normally observed in the absence of oily contamination.

It is obvious from this discussion that to minimize the chance of a titanium reaction when titanium and its alloys are exposed to hydrogen gas, the following precautions and treatments should be taken:

- (1) Protect the material from all abrasion or galling of the surface during fabrication.
- (2) Keep oil and other contaminants from contact with the material. This includes fingerprints.
- (3) Before use, degrease thoroughly and pickle in a solution of 67 parts  $H_2O$ , 33 parts  $HNO_3$ , and 3 parts HF. A significant amount of metal removal is desirable. A 2-mil surface layer removed in the present work was effective in eliminating reaction with hydrogen.
- (4) During use, refrain from handling with the bare hands and prevent any scratching or abrasion of the surface.

### Conclusions

It is apparent that a reaction between hydrogen gas and titanium to form titanium hydride is possible at room temperature. The occurrence of this reaction is affected by a number of variables acting in a complex manner. As a result, small differences in experimental technique can prevent a reaction where one is normally expected or cause a reaction when none is expected.

During the course of the present studies, several factors were found to favor the occurrence of a reaction. These included increased hydrogen pressure, increased reaction temperature, abrasion of the titanium surface immediately before exposure to hydrogen (at pressures above two atmospheres), vacuum annealing at 1500 F to dissolve surface oxides before hydrogen exposure, and galling of the surface with other materials such as iron or titanium alloys, especially if galling occurred in the presence of oil. Microstructure and alloy composition also affected the reaction. The amount of hydriding under a given set of conditions was greater for acicular than for equiaxed structures. Ti-5Al-2.5Sn and unalloyed titanium seemed more reactive than Ti-6Al-4V. All alloys and all microstructural conditions examined reacted, however.

Stress was expected to favor the hydriding reaction either by causing cracking of the thin oxide surface layer or by causing the hydride to spall rapidly as it formed, thus continuously exposing clean metal. This was not found to be the case, however. In only one case was stress found to cause hydride spalling and pitting, a sample of Ti-6Al-4V exposed to fatigue loading. Several similarly loaded samples did not develop pitting, however. As a means of inducing oxide cracking, several samples were oxidized at elevated temperatures to develop thicker, more brittle oxide layers. The rate of hydriding of those samples was also unaffected by stress.

Factors which appeared to inhibit or prevent a hydriding reaction were impurities in the gas phase, exposure to air for several days after surface treatments involving abrasion or galling, which favor the reaction, and pickling in a  $\text{HF:HNO}_3:\text{H}_2\text{O}$  solution to remove measurable amounts of surface metals. The effectiveness of these factors in preventing a reaction is difficult to assess with certainty.

Although a reaction was never observed in the present work unless liquid nitrogen cold trapped hydrogen was used and unless the reaction vessel was evacuated to about 1 micron pressure or less before hydrogen was introduced, it is not certain that small changes in technique would not cause a reaction to proceed in a less pure hydrogen atmosphere. The need for a high-purity gas phase is undoubtedly related to the amount of titanium surface available for reaction as shown by studies using titanium gettered at one atmosphere pressure. In the present studies, the ratio of gas volume to metal surface was quite high.

From the studies conducted in this work, it is possible to point to several factors which may have favored the hydriding reaction leading to failure in the hydrogen tank described in the Introduction. These are:

- (1) The high-purity hydrogen gas phase existing over liquid hydrogen.
- (2) The galling of the tube inner surface by the mandrel used in tube drawing.
- (3) The galling and abrasion of the tube ends by wire brushing prior to welding of the attachment fittings.

- (4) The microstructural changes occurring in the weld region.
- (5) The moderately high hydrogen pressure (greater than 2 atmospheres).

Although less clearly demonstrated by this study, it seems probable that thermal cycling was also a factor in the hydride spalling and rapid pitting leading to perforation of the tubing.

Based upon the studies performed during this program, the use of titanium alloys in a hydrogen atmosphere at room temperature must be approached with caution. A hydriding reaction can occur, and in certain cases, can proceed quite rapidly causing severe pitting or conversion of major amounts of material to hydride.

#### STUDIES OF WELD EMBRITTLEMENT RESULTING FROM HYDROGEN SEGREGATION

##### Introduction

A helium pressure vessel constructed of heat treated Ti-6Al-4V failed leading to the destruction of a Saturn S-IV B rocket during a test sequence. Unalloyed titanium filler was inadvertently used in making the tank girth weld, a multipass weld joining 0.4-inch-thick hemispheres. Moreover, although both the unalloyed filler metal and the Ti-6Al-4V hemispheres contained less than 100 ppm hydrogen, extensive hydride segregation was found at the weld metal:heat affected zone interface. A major composition change also occurred at this point, the composition changing from essentially pure titanium to Ti-6Al-4V. Since the tank had survived proof testing at pressures well above the service pressure, it appeared that failure may have resulted from hydride precipitation during service rather than from low weld strength, and that the use of unalloyed titanium filler was a contributing factor rather than the direct cause of failure.

The use of unalloyed filler in the welding of Ti-6Al-4V is common practice. However, there is usually a significant amount of weld dilution, such that the weld metal contains appreciable aluminum and vanadium after welding, and no weld failures attributed to hydride formation in this type of weldment have been reported. Nevertheless, the failure cited above indicated the need for an investigation of the conditions leading to hydride formation in Ti-6Al-4V weldments made with unalloyed filler metal. Factors of importance were considered to be hydrogen content of components, amount of weld dilution, and post-weld heat treatments. A program was initiated to examine in a preliminary manner the effects of these variables on hydride formation and weldment properties.

### Material

Ti-50A and Ti-6Al-4V materials were obtained from Titanium Metals Corporation of America (TMCA). Both were in the form of 0.125-inch sheet, 36 inches in length. The Ti-50A was 2 inches wide, the Ti-6Al-4V, 4 inches wide. The analyses are shown in Table 28.

It was necessary to hydrogenate and heat treat the Ti-6Al-4V to produce the desired hydrogen contents of 50 and 150 ppm and microstructure of 50 percent equiaxed alpha. The heat treatment procedure which was performed after hydrogenation was as follows:

- (1) Solution heat treat for 10 minutes at 1740 F in air.
- (2) Water quench.
- (3) Surface grind to remove 3 mils per side.
- (4) Age between clamped stainless steel plates (to flatten) for 1-1/2 hours at 1000 F and air cool.
- (5) Pickle lightly.
- (6) After welding, age for 2-1/2 hours at 1000 F between clamped stainless steel plates and air cool.

The Ti-50A was degreased thoroughly and used with no annealing treatment other than that applied during hydrogenation.

All material was cut into 18-inch lengths for easier accommodations in the equipment which was used for the hydrogen addition.

### Experimental Procedures

In order to obtain the necessary hydrogen levels, plates of both Ti-50A and Ti-6Al-4V were hydrogenated by exposure to gaseous hydrogen at elevated temperatures. The plates (3 were hydrogenated simultaneously) were sealed inside a 304 stainless steel tube 5 feet in length by 4-3/4 inch ID with 1/8-inch walls, one end of which was welded closed and the other, through which the plates were inserted, was closed by a stainless steel flange and copper gasket. The tube was attached to the same glass modified Sieverts apparatus described in the first phase of this work, Figure 4. The plates were heated to 1350-1400 F by two 8-foot by 2-3/4-inch wide heating tapes wound on the outside of the 5-foot tube and heavily insulated with asbestos and fiber glass. Calculated quantities of hydrogen were added from a calibrated volume (not shown in Figure 4). The progress of the hydrogenization was followed with a mercury manometer. After absorption of the added hydrogen, usually in 15 to 30 minutes, the plates were maintained at temperature for one to two additional hours to allow for homogenization of the hydrogen in the material, then cooled slowly to room temperature.



TABLE 28. ANALYSES OF THE Ti-50A AND Ti-6Al-4V SHEET

Material	Heat Number	Percent by Weight						
		C	Fe	Al	V	H	O	N
Ti-50A	G5411	0.022	0.10	--	--	0.0030	0.11	0.008
Ti-6Al-4V (a)	G5398	0.025	0.10	5.0	4.3	0.0030	0.10	0.015
	G4820	0.026	0.11	6.0	4.1	0.0050	0.11	0.014

(a) Two heats of the same material were received.

The attainment of the desired hydrogen levels in this equipment proved unexpectedly difficult. A total of 20 sheets of Ti-6Al-4V and 6 sheets of Ti-50A were hydrogenated; however, only 11 sheets of Ti-6Al-4V and 4 sheets of Ti-50A filler were used because of a change in program plan made at a later stage in the investigation. Initially, spot checking of hydrogen contents was planned. However, as occasional high hydrogen plates were found, a more complete hydrogen analysis program was instituted. Unfortunately, one high hydrogen plate was included in a weldment before it was discovered to be off analysis. Although this weldment was carried through the test program, metallographic examination and notch location in notched testing was restricted to the half of the weldment showing an acceptable hydrogen content.

It was originally planned to prepare fourteen weldments according to the schedule shown in Table 29. These weldments were to include four combinations of hydrogen content in unalloyed filler metal and Ti-6Al-4V base metal. Weldments 1 through 12, and two weldments at high hydrogen levels made with either Ti-6Al-4V or Ti-5Al-2.5Sn filler metal, Weldments 13 and 14. It was planned that the first 12 weldments would include three levels of weld dilution for each combination of hydrogen content: low ( $\sim 0$ ), medium ( $\sim 30$ ), and high ( $> 50$ ). Weld dilution was calculated as follows:

$$\frac{B}{A + B} \times 100 = \text{percent weld dilution}^*$$

where B is the volume of filler metal and A is the volume of base metal in the weld metal zone.

While hydrogenation and heat treatment of material was in progress, work was initiated on development of weld procedures to control weld dilution. Despite extensive variations in welding conditions and joint design, it was not possible to obtain a weld dilution level of less than 35 percent while obtaining complete weld fusion. Moreover, it was not possible to increase the alloy content of the filler metal much above the 35 percent level without creating an excessively large weld bead. As a result, it was decided to discontinue efforts to produce the majority of the weldments in Table 29 and to concentrate upon evaluation of five medium dilution weldments, Nos. 2, 5, 8, 11, and 13. The hydrogen contents of these medium dilution weldments are shown in Table 30. As shown here, the hydrogen content of most components of these weldments was somewhat higher than the desired level.

The titanium alloy plates were welded using the gas tungsten arc process in a vacuum-purged argon back-filled welding chamber. The chamber is equipped with a mechanical pump which can evacuate the chamber to less than 5 microns pressure before back-filling the chamber. The chamber is also equipped with a movable work table controlled by a calibrated servo-controlled motor and gear box to provide precise control of the travel speed.

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\* This formula is that used by the American Welding Society, Welding Handbook, 6th Edition, Section 1, p 2.37.

TABLE 29. VARIABLES TO BE EXAMINED IN WELDED SHEET

Weldment No. (a)	Hydrogen Content of Ti-6Al-4V Sheet	Filler Metal Composition	Hydrogen Content of Filler	Degree of Weld Dilution
1	~ 50 ppm	Ti-50A	~ 50 ppm	Low
2	"	"	"	Medium
3	"	"	"	High
4	~ 150 ppm	"	"	Low
5	"	"	"	Medium
6	"	"	"	High
7	"	"	~ 150 ppm	Low
8	"	"	"	Medium
9	"	"	"	High
10	~ 50 ppm	"	"	Low
11	"	"	"	Medium
12	"	"	"	High
13	~ 150 ppm	Ti-6Al-4V	"	Low
14	"	Ti-5Al-2.5Sn	"	Low

(a) Two 4 x 18-inch sheets to be joined along the 18-inch dimension to produce an 8 x 18-inch weldment.

TABLE 30. HYDROGEN CONTENT OF MEDIUM DILUTION WELDMENTS

Weldment Number	Hydrogen Content of Ti-6Al-4V Sheet, ppm		Hydrogen Content of Ti-50 Filler, ppm	
	Desired	Actual	Desired	Actual
2(a)	50	63	50	64
	50	--		
5(b)	150	189	50	64
	150	188		
8(b)	150	192	150	145
	150	313		
11(a)	50	72	150	145
	50	--		
13(b)	150	170	150 <sup>(c)</sup>	136
	150	178		

(a) Ti-6Al-4V plate from Heat G4820 used for this weldment.

(b) Ti-6Al-4V plate from Heat G5398 used for this weldment.

(c) Ti-6Al-4V filler metal for this weldment was from Heat G5398.

An automatic constant voltage controlled welding head, which maintains the proper arc length, and a DC power supply with a high frequency start capability was used in this work.

Each welded plate was made from two 18 x 4-inch titanium plates surface ground to a thickness of 0.110 inch and one 20 x 1/4 x 1/8-inch titanium insert. The insert constituted the filler metal. A double 45-degree bevel was machined along one 18-inch edge of each plate. The other 18-inch edge was faced off so that the total width of each pair of plates was exactly 4 inches.

Figure 22 shows, schematically, the joint configuration and tooling.

The insert was placed between the 45-degree bevels of each plate. Two copper bars were used to provide a controlled chill and hold down tooling for the assembly. The bars were placed about 1 inch from the weld center line. Steel hold-down clamps were placed about every six inches along the length of the chill bars to provide the hold-down force.

Tooling at the bottom of the joint consisted of a copper backing plate inserted into the work table. The backing plate provided the bottom chill and was machined flush with the top of the work table. A 2-inch side x 1/4-inch deep slot was machined into the backing plate so that it was not in contact with the filler metal insert or titanium plate near the weld area.

The vertical position of the filler metal insert was obtained by placing three small copper shims along the insert length between the insert and the backing plate. At these same locations on the top, steel bars containing a screw were used to clamp the insert into position.

The titanium alloy plates and filler metal insert were inserted into the chamber and the tooling was clamped into place. The table was then slowly moved from end to end to check for proper alignment of the tungsten electrode along the insert center line. After final alignment, the chamber was then purged and back-filled with the high-purity argon to a slight positive pressure. Tack welds were then placed in the middle and at each end of the insert. The insert positioning clamps and copper shims were removed and the tacked assembly reclamped and realigned. The top weld was then made along the length of the plates. The first pass melted the top portion of the insert achieving about 55 percent penetration. The partially welded assembly was then removed from the tooling, rotated 180 degrees about the longitudinal weld axis, reclamped, and realigned. The second pass weld was then made to complete the joint.

The range of the welding parameters for each pass as indicated by a recording volt ammeter are shown in Table 31 along with other parameter information.

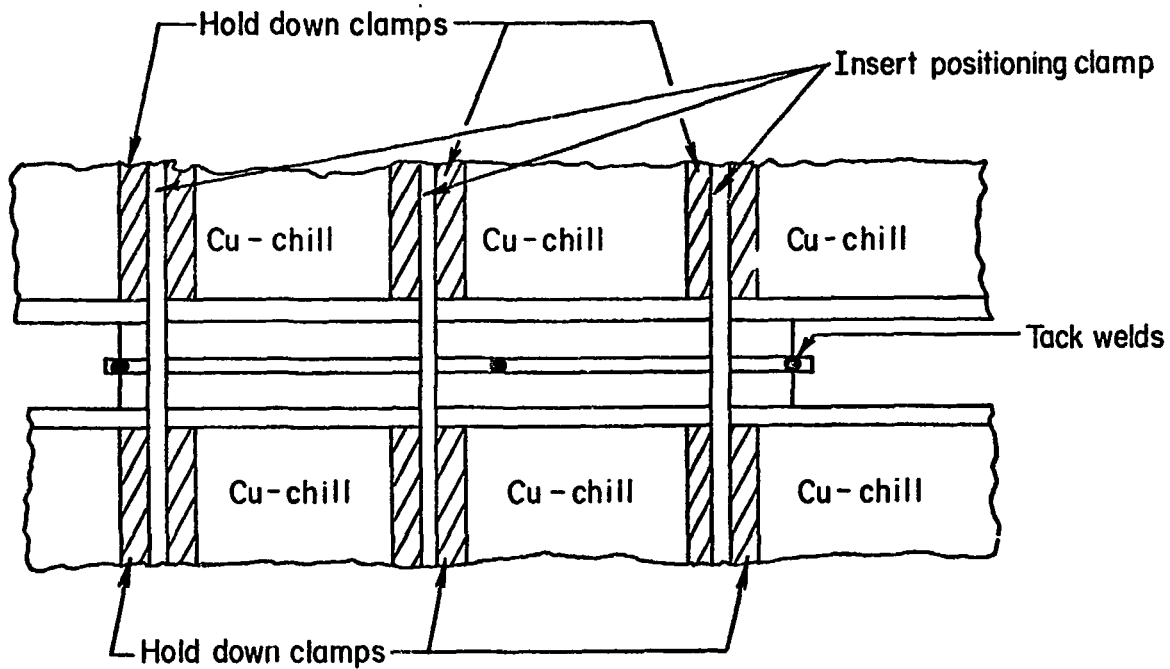
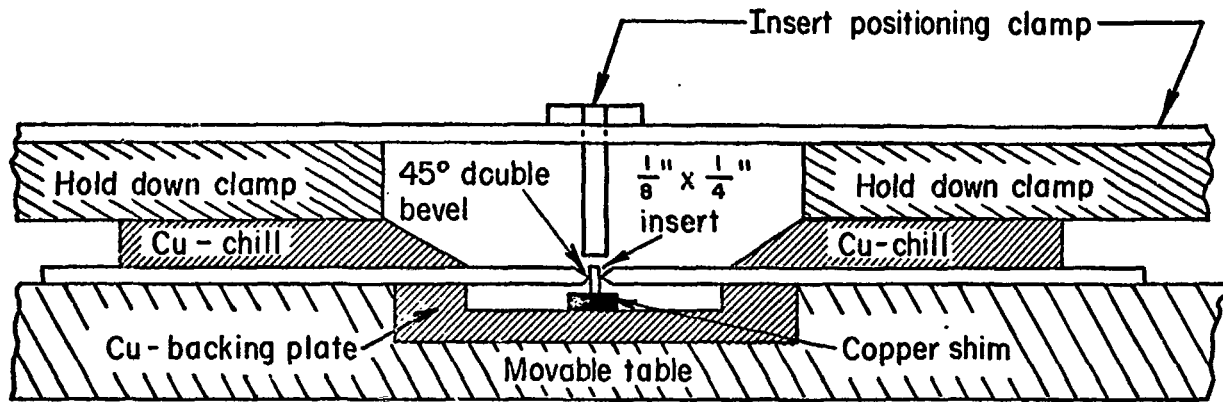


FIGURE 22. JOINT CONFIGURATION AND TOOLING  
FOR PRODUCTION OF THE WELDMENTS

TABLE 31. WELDING PARAMETERS

	1st Pass	2nd Pass
Arc Voltage (volts)	13-14	13-14
Weld Current (amps)	159-160	159-160
Travel Speed (inch/minute)	8	8
Electrode (negative)	3/32-inch diameter--1%	Thoriated Tungsten
Electrode Stickout (inch)	3/4	3/4

This technique resulted in a weld dilution of approximately 35 percent when using unalloyed titanium filler. Analysis of the weld metal showed it to contain approximately 2.0 percent aluminum and 1.4 percent vanadium.\*

Upon completion of the welding, the welded plates were aged an additional 2-1/2 hours at 1000 F in air and air cooled, then ground flat. Test samples were cut from the plates as shown in Figure 23 to provide material for constrained bend, tensile, notched tensile, notched stress rupture, and metallographic tests. Constrained bend samples measured 3/4 x 8 inches and were fastened onto a radiused steel mandrel to provide a maximum surface strain of 0.33 percent. Notched tensile and stress rupture samples were machined to provide a stress concentration factor ( $K_t$ ) of 6 as shown in Figure 23b. The notch was located in the weldment, such that the root of the notch was offset slightly from the center line of the weld nugget (see Figure 23b). The notch cut through regions of weld metal and heat affected zone and in some locations coincided with the hydride. Unnotched tensile samples were machined according to the drawing in Figure 23c.

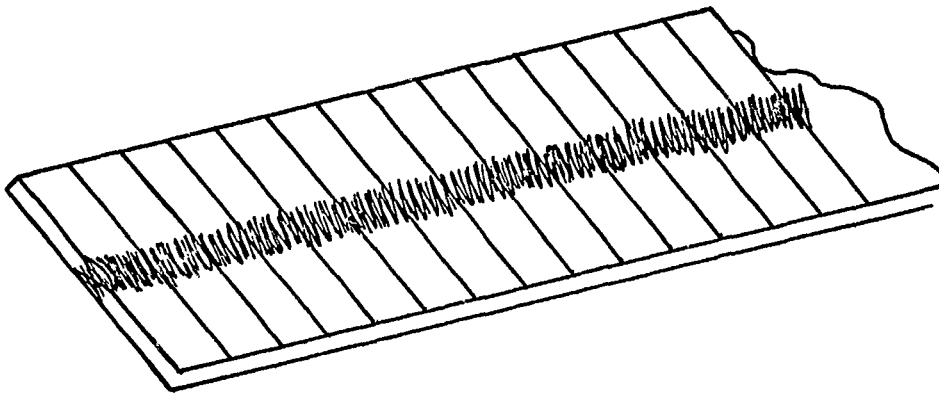
### Results

Because of the significant weld dilution which was present in these samples, segregation of hydrogen was not expected. However, as shown in Figure 24, several of the welds showed obvious hydrogen segregation appearing as bands of hydride along portions of the fusion zone-heat affect zone interface. Banding was evident only along the interface formed in the second weld pass. The banding along this interface was most prominent in Weldment 8 where both the base plate and filler metal were high in hydrogen (Figure 24c). Weldment 5, made with low hydrogen filler metal and high hydrogen base plate, also showed obvious banding (Figure 24b). Only a slight indication of banding is seen on the two welds made with unalloyed filler metal and low hydrogen base plate, Weldments 2 and 11 (Figure 24a and 24d) while no hydride was seen in Weldment 13 made with Ti-6Al-4V filler metal even though both base plate and filler metal contained high hydrogen contents (Figure 24e). The amount of hydride distributed through the weld nugget appeared to decrease in the following order: 8 (Figure 24c), 5 (Figure 24b), 11 (Figure 24d), 2 (Figure 24a), and 13 (Figure 24e). Since the hydrogen content was initially over twice as high in the filler metal used to make Weldments 8 and 11 as in the filler metal used to make Weldments 2 and 5, it appears that significant hydrogen passed from the base plate to the weld metal during welding to cause the large amount of hydride observed in Weldment 5. As will be noted later, it is possible that Weldment 5 was contaminated slightly during welding, and this factor may have contributed to the larger than expected amount of hydride formation. The absence of hydrides in Weldment 13 is due to the high solubility of hydrogen in Ti-6Al-4V.

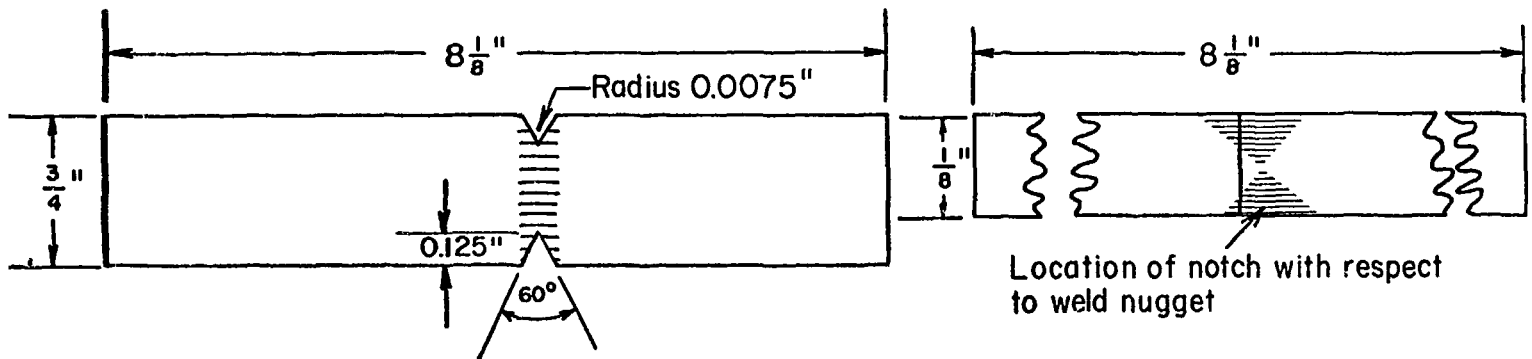
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\* Measurements of weld dilution were made only on test welds. Since it was found that weld dilution was reasonably constant with the technique used, it was considered unnecessary to run analyses on the five weldments prepared for mechanical property studies.

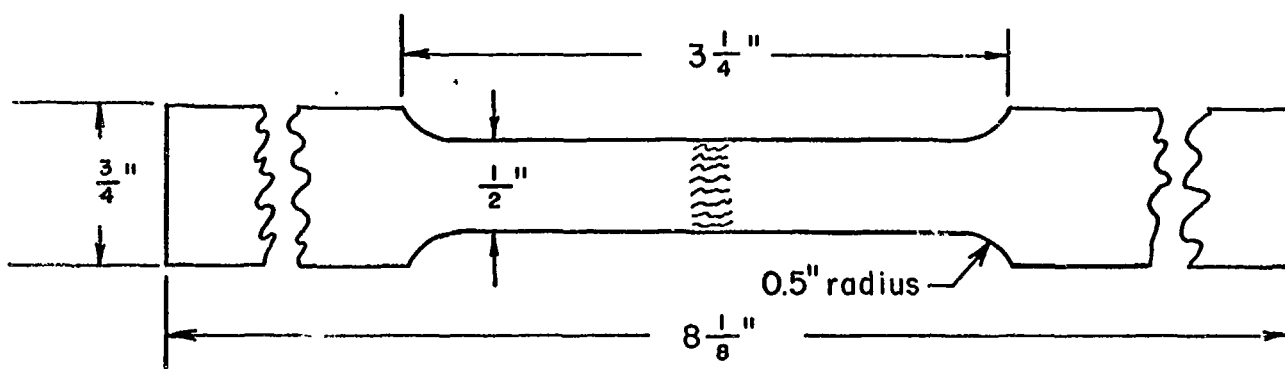




a. Sample Blank Cutting Procedure

b. Notched Test Sample ( $K_t = 6$ )

Side view of weld

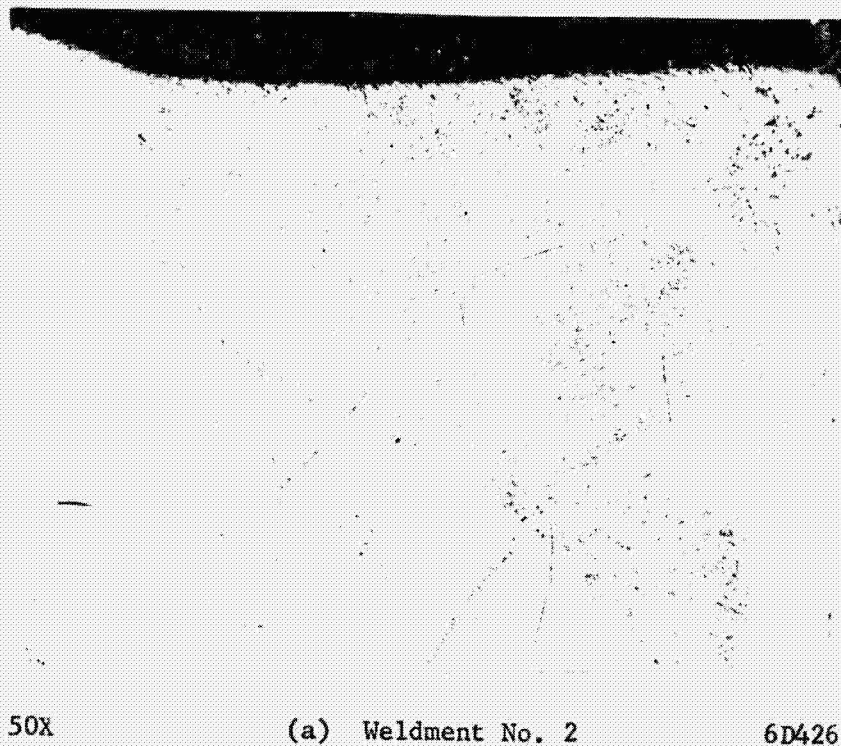


c. Unnotched Test Sample

FIGURE 23. TEST SAMPLE LOCATION AND SAMPLE DIMENSION

Base Plate  
Ti-6Al-4V  
65 ppm H<sub>2</sub>

Filler  
Ti-50A  
65 ppm H<sub>2</sub>



Base Plate  
Ti-6Al-4V  
190 ppm H<sub>2</sub>

Filler  
Ti-50A  
65 ppm H<sub>2</sub>

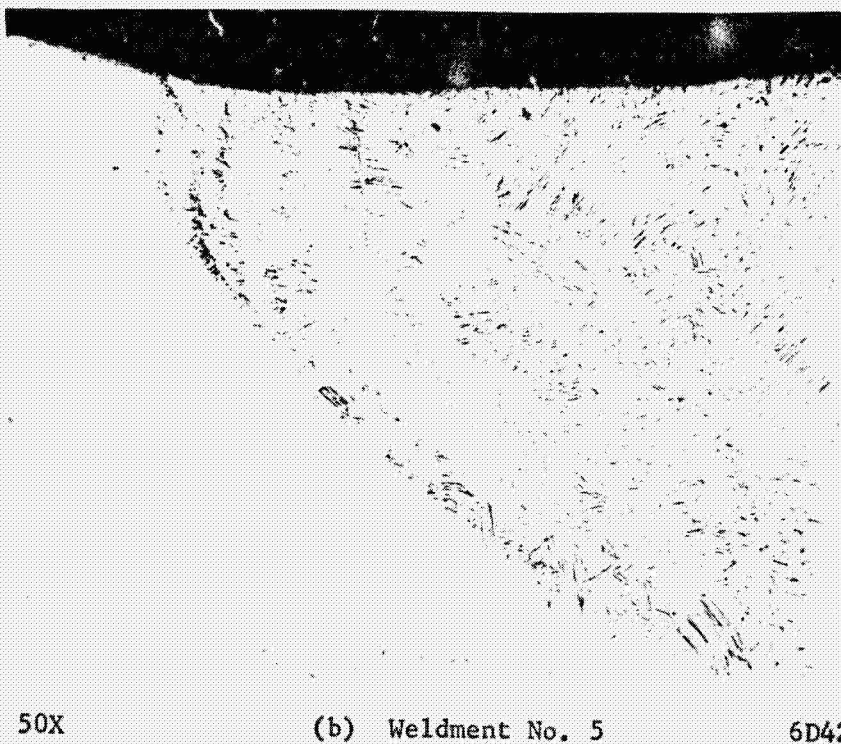


FIGURE 24. HYDRIDE PRECIPITATED IN WELD AREA

Ti-6Al-4V plate is to the left, Ti-50A  
filler metal to the right.

Base Plate  
Ti-6Al-4V  
190 ppm H<sub>2</sub>

Filler  
Ti-50A  
145 ppm H<sub>2</sub>



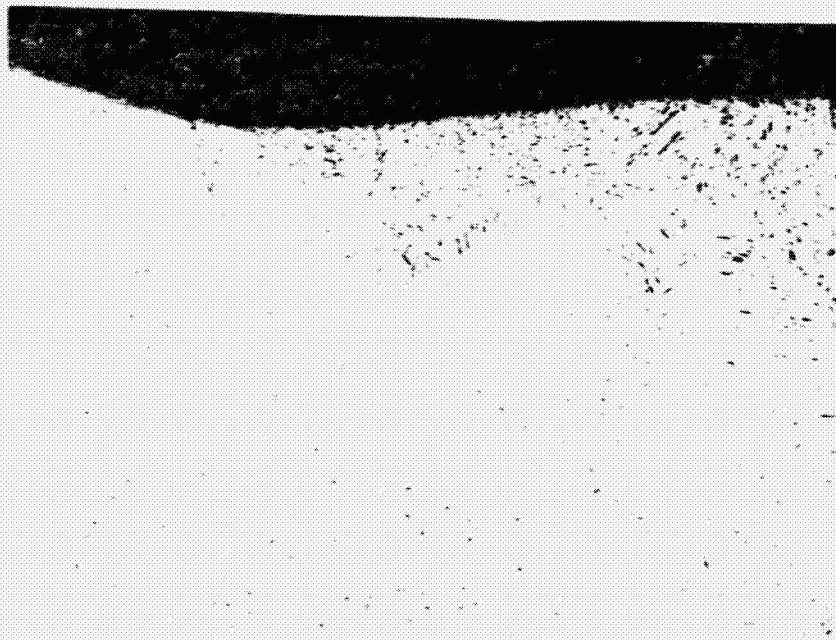
50X

(c) Weldment No. 8

6D425

Base Plate  
Ti-6Al-4V  
70 ppm H<sub>2</sub>

Filler  
Ti-50A  
145 ppm H<sub>2</sub>



50X

(d) Weldment No. 11

6D428

FIGURE 24. (continued)

Base Plate  
Ti-6Al-4V  
170 ppm H<sub>2</sub>



Filler  
Ti-6Al-4V  
135 ppm H<sub>2</sub>

50X

(e) Weldment No. 13

6D427

FIGURE 24. (continued)

When hydrides are present in titanium alloys, they normally result in a loss in tensile ductility in high strain rate unnotched tensile tests and a loss in tensile strength and ductility in notched tensile tests. This type of embrittlement is known as impact embrittlement. Unnotched tensile tests were run at two cross head speeds, slow (0.005 inch per minute to yielding and 0.05 inch per minute to failure) and fast (0.5 inch per minute), and notched tensile tests were run at 0.005 inch per minute in an effort to detect impact embrittlement. All tests were conducted at room temperature.

The results of duplicate unnotched tensile tests performed at a slow testing rate are shown in Table 32. It is seen that Weldment 2, in which both filler metal and base plate were low in hydrogen, has the highest ductility of the four weldments made with unalloyed filler. Weldment 13, made with Ti-6Al-4V filler, shows considerably higher strength than the other four weldments, as would be expected, and also shows good ductility. Weldment 5 shows a higher ultimate strength and lower reduction in area than Weldments 2, 8, or 11. This is tentatively attributed to slight oxygen contamination during welding. If the yield strength of Weldment 5 is also assumed to have been increased by contamination, perhaps as much as 3000 psi higher than it would normally have been, Weldment 2 is seen to have the highest yield strength of the four weldments made with unalloyed filler metal. Except for slight differences in ductility and possibly yield strength, the hydride distribution had little effect on tensile properties at a slow testing speed.

The results of duplicate unnotched tensile tests performed at a fast testing speed are shown in Table 33. As was observed in slow tensile tests, Weldment 5 was somewhat stronger and less ductile than Weldments 2, 8, or 11, while Weldment 13 was considerably stronger than the other four. The ductility differences between the four weldments made with unalloyed filler are small except for the reduction in area of Weldment 5 and probably are not significant, although the two weldments showing obvious hydride banding, Nos. 5 and 8, were the least ductile. Some contamination of Weldment 5 is also indicated by the tensile data attained at a fast strain rate.

The results of duplicate notched tensile tests are shown in Table 34. In these tests, the ductility correlated with the metallographic observations for the four weldments made using unalloyed filler metal. Moreover, the notched strength and the notched:unnotched strength ratio suggested that Weldment No. 2, in which both base plate and filler metal were low in hydrogen, was superior to the other three. These differences were quite small, however. Weldment 13, made with Ti-6Al-4V filler, was more notch sensitive than any of the weldments made with unalloyed filler as indicated by a lower notched:unnotched strength ratio.

It was obvious from these tests that the hydride present in the weldments had little effect on tensile properties. There was no evidence of significant impact embrittlement. Since the tank failure discussed in the Introduction occurred after considerable service under stress, it was considered possible that additional hydride precipitation or hydride agglomeration might occur during prolonged loading, that is, that the weldments would be susceptible to the type of hydrogen embrittlement referred to as low strain rate embrittlement. Two test procedures were used to detect low strain rate embrittlement, notched stress rupture tests and constrained bend tests.

TABLE 32. RESULTS OF UNNOTCHED TENSILE TESTS  
PERFORMED AT A SLOW TEST RATE<sup>(a)</sup>

Weldment Number	Ultimate Strength, psi	Yield Strength, psi	Percent Elongation <sup>(b)</sup>	Reduction in Area, percent
2	102,000	88,400	5.5	34
	<u>101,200</u>	<u>89,600</u>	<u>5.0</u>	<u>32</u>
Average	101,600	89,000	5.2	33
5	104,200	89,600	5.0	24
	<u>104,800</u>	<u>89,900</u>	<u>4.0</u>	<u>26</u>
Average	104,500	89,800	4.5	25
8	98,900	84,300	4.0	27
	<u>102,300</u>	<u>89,000</u>	<u>4.0</u>	<u>31</u>
Average	100,600	86,600	4.0	29
11	101,200	86,400	4.5	31
	<u>100,300</u>	<u>84,900</u>	<u>4.5</u>	<u>29</u>
Average	100,800	85,600	4.5	30
13	141,500	123,500	5.0	23
	<u>141,900</u>	<u>123,400</u>	<u>4.5</u>	<u>16</u>
Average	141,700	123,400	4.8	20

(a) Cross head speed of 0.005 inch per minute to yield, then 0.05 inch per minute to failure.

(b) Measured between 2-inch gage marks. All samples fractured in weld metal.

TABLE 33. RESULTS OF UNNOTCHED TENSILE TESTS  
PERFORMED AT 0.5 INCH PER MINUTE

Weldment No. (a)	Tensile Strength, psi	Percent Elongation (a)	Reduction in Area, percent
2	106,500	5	32
	<u>104,600</u>	<u>5</u>	<u>36</u>
Average	105,600	5	34
5	109,600	4	19
	<u>110,400</u>	<u>4</u>	<u>18</u>
Average	110,000	4	18
8	104,600	5	29
	<u>106,000</u>	<u>4</u>	<u>28</u>
Average	105,300	4.5	28
11	105,400	5	37
	<u>105,800</u>	<u>5</u>	<u>35</u>
Average	105,600	5	36
13	148,900	5	24
	<u>147,700</u>	<u>5</u>	<u>20</u>
Average	148,300	5	22

(a) Measured between 2-inch gage marks. All samples fractured in weld metal.

TABLE 34. RESULTS OF NOTCHED TENSILE TESTS ( $K_t = 6$ )

Weldment Number	Notched Tensile Strength, psi	Percent Elongation <sup>(b)</sup>	Notched:Unnotched Strength Ratio <sup>(a)</sup>
2	119,800	4	
	<u>116,500</u>	<u>3</u>	
Average	118,200	3.5	1.16
5	117,200	3	
	<u>118,700</u>	<u>3</u>	
Average	118,000	3.0	1.13
8	112,600	2	
	<u>115,300</u>	<u>3</u>	
Average	114,000	2.5	1.13
11	113,200	3	
	<u>114,700</u>	<u>3</u>	
Average	114,000	3.0	1.13
13	153,000	3	
	<u>147,100</u>	<u>1</u>	
Average	150,000	2.0	1.06

(a) Based on comparisons with the results of unnotched tensile tests run at a slow strain rate (Table 32).

(b) Measured between 1/2-inch gage marks.



The results of notched stress rupture tests on the five weldments are presented in Table 35 and plotted in Figure 25. Although there is some scatter in the data, it appears that all four of the weldments made with unalloyed filler had approximately the same 100-hour rupture strength, about 95,000 psi, while the rupture strength of the weldment made with Ti-6Al-4V was about 25,000 psi higher. Samples from Weldments 8 and 5 failed in tests at 97,000 psi, while samples from Weldments 2 and 11 did not fail within 100 hours. A sample of Weldment 8 was also placed in test at 96,000 psi and failed in 37 hours. However, as shown in Figure 25, these results are well within the normal scatter band of a single rupture curve including data from all four weldments made with unalloyed filler metal. Low strain rate embrittlement is not an obvious factor in these results.

Sustained load bend tests were run in two ways. In the first tests, a sample of each weldment was fastened to a curved steel block at room temperature. The radius of the block was such that the sample outer fibers were strained in tension 0.33 percent transverse to the weld. In the second test, both the block and the sample were heated to 400 F for 17 hours, the samples were attached to the steel block, and the strained samples and test block were cooled to room temperature. In all cases, the second weld pass was placed in tension. It was hoped that moderate heating followed by slow cooling under stress would accelerate hydrogen redistribution. Both groups of samples were examined periodically for cracks in the weld regions using the Zyglo technique, but none were found. The samples stressed at room temperature were held in test for 51 days. Those stressed at 400 F were held in test at room temperature for 23 days.

The results of the notched stress rupture and sustained load bend tests showed no evidence of low strain rate embrittlement. Since the notch stress rupture test is quite sensitive to low strain rate embrittlement tendencies, it is concluded that these weldments are not susceptible to low strain rate embrittlement. This was not unexpected since most of the hydrogen present was obviously already precipitated in the form of hydrides. Only that portion in solution can contribute to strain rate embrittlement.

Despite the failure to detect evidence of significant embrittlement in these weldments, the observation that a major segregation tendency existed in weldments involving Ti-6Al-4V plate and unalloyed titanium filler, even when a moderate amount of weld dilution was present, is disturbing. Hydride banding of the type observed, although apparently not harmful in the weldments studied, is likely to prove quite damaging if it becomes much more extensive. Further study of the factors leading to hydride banding and its effect on properties are needed.

### Conclusions

When Ti-6Al-4V plate is welded with unalloyed filler wire, a tendency for hydrogen redistribution between the base plate and filler metal exists. Bands of hydride were present along the fusion zone:heat affected zone interface in two of five weldments prepared in this study.

TABLE 35. RESULTS OF NOTCHED STRESS  
RUPTURE TESTS PERFORMED AT  
ROOM TEMPERATURE

Weldment Number	Stress, psi	Time to Failure, hr
2	111,900	0.2
	105,600	0.7
	97,000	112.4 discontinued
5	116,600	0.01
	110,000	0.3
	97,000	92.5
8	111,600	0.03
	100,000	43.6
	97,000	3.0
	96,000	37.0
11	111,900	0.05
	100,300	6.4
	97,000	100.0 discontinued
13	148,300	0.06
	133,500	0.10
	120,000	100.0 discontinued

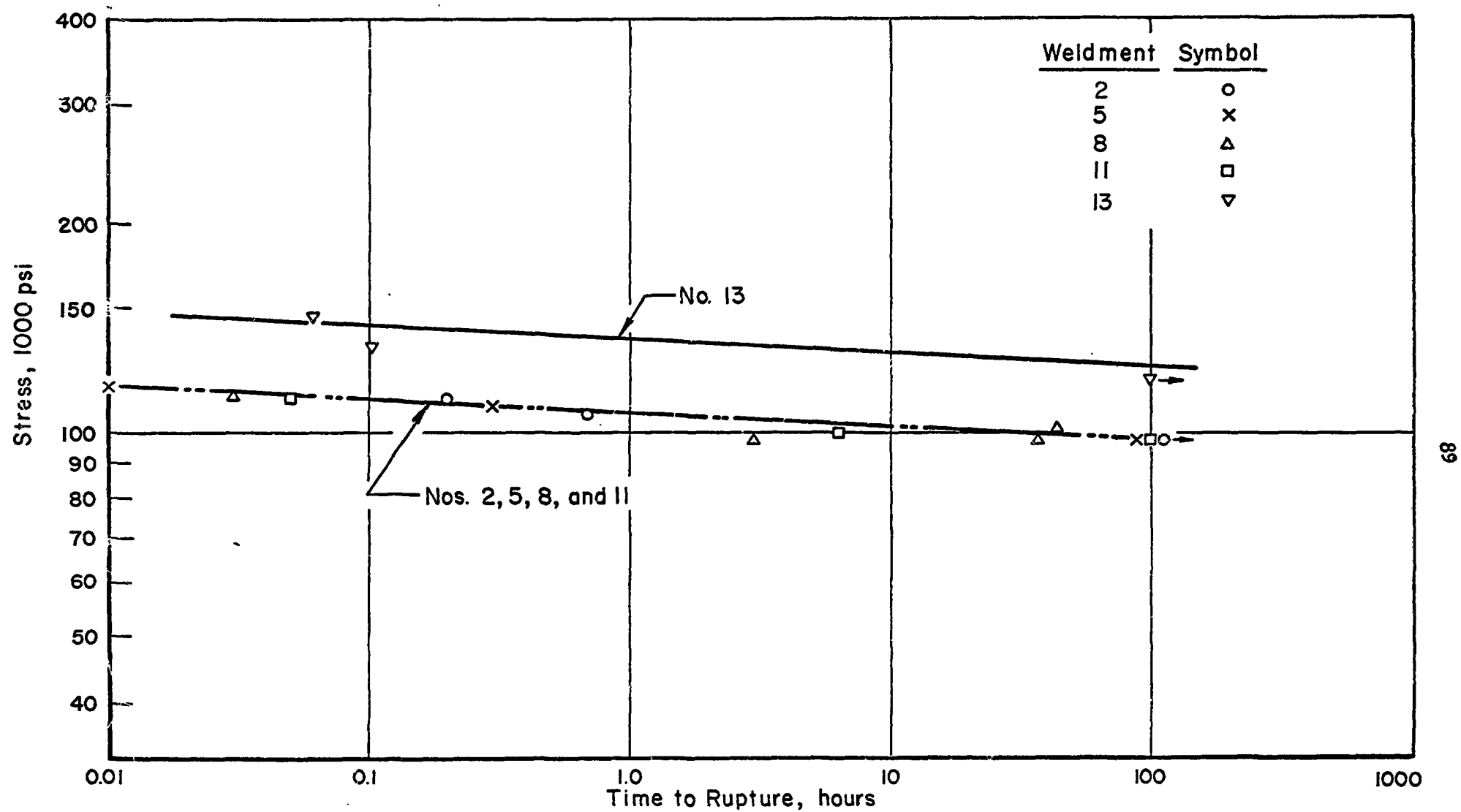


FIGURE 25. STRESS RUPTURE CURVES FOR NOTCHED SHEET SAMPLES AT ROOM TEMPERATURE